S. P. L. Sörensen.

THE DETERMINATION

OF

HYDROGEN IONS

An elementary treatise on electrode, indicator and
supplementary methods with an indexed
bibliography on applications

BY

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To
Fellow Workers in the Biological Sciences,
Architects of Progress,
Who Hew the Stone to Build Where Unseen Spires Shall Stand

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PREFACE TO THE THIRD EDITION

Within the past twenty years methods of determining hydrion concentration have served well in the exploration of many and divers subjects. But the period of general exploration is drawing to a close and long ago there were begun exact studies of equilibria, or of kinetic events in which hydrions participate. Refinement of technique, variety of method and elegance of formulation are in greater demand. Accordingly there have been added in this edition chapters or sections bearing upon each of these aspects, and the old text has been almost entirely rewritten to conform to the revised presentation. There results a superficial appearance as of a more exhaustive treatment. However, the requirements of a new age have far outrun the range of subject and the depth of treatment that can be encompassed with adherence to the more or less discoursive style of presentation which it has seemed best to use. Consequently this enlarged edition remains more elementary in relation to the needs of today than was the first edition in relation to the needs of its period.

The expansion has not led to a wholly satisfactory product. For the faults of comprehension or of exposition I need ask no charity. It cannot, or should not, be given in such matters. But I feel compelled to shift to *the times* some responsibility for one or two of the major faults of this book.

So varied and extensive are the applications of the methods, the details of technique and the special forms of theory that it is become about as ridiculous to attempt to recount all aspects within one text as it would be to note all the uses of the thermometer, all types of data to which is affixed the symbol °C. and at the same time to exhaust the theory of thermometry. But, having set out to glean from the literature important information which I think is still desired in one text, I believe the reader will be interested in a survey incidental to this task and described by the accompanying chart.

The data were compiled as follows. The number of papers for each of the years from 1910 to 1920 was taken from the bibli-

ography of the second edition. Estimates for each of the subsequent years were made as follows. Several numbers of Chemical Abstracts for each year were taken at random and carefully searched in *all* sections for papers which seemed to conform to the types included in the bibliography of the second edition. From the number of pages searched and the number of pages for the year the number of such articles for that year was calculated. Of course, a serious question of personal judgment enters. This need not be discussed, for I trust the reader to recognize in the chart what he himself must have felt is happening in his own specialty.
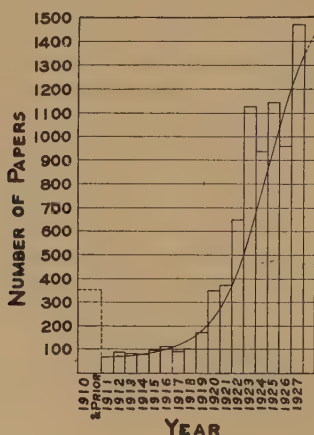
The situation has made obsolete some of the old ideals of scholarship. It has made trivial all available facilities of library, abstract and review. It has made the monograph almost futile. It has made ridiculous him who claims to combine thorough investigation with thorough *re*-search.

Undoubtedly the mediaeval scholar felt oppressed by the magnitude of his specialty in his time and looked forward with misgiving to the "impossible" tasks of the future; and yet, with no vacation such as Sir Ernest Rutherford whimsically prays for as a need of the present, scholarship survived then and doubtless will now. However, there was one disease of mediaeval times that had to be cured before the intellect came to renewed health and to vigor adequate for enlarged tasks. I fear that we may be

reinfected. It was the pursuit of "vanishing particulars" and the employment of conveniences suited to a purpose. A new age has brought new purposes and an equal sincerity of a new type that makes us sometimes scorn the old; but amid the abundance of our learning the instinct of mastery has driven us to take refuge in specialization wherein we are at liberty to make our neighbors the victims of our conveniences. They are the conveniences of special terminologies suited to the immediate need of the specialist but barriers to earnest seekers of the contents of the specialty. They are the conveniences of special formulations suited to the immediate needs of the case but barriers to the widespread use of the meaning of the case. While I have tried to avoid, so far as possible, discussion of the less significant instances, I conceive it to be the function of this book to tell *about* a few of the more important matters in terms agreeing essentially with those which the reader will have to know in his study of the literature. Partly because the literature is what it is, the subject is not here presented as I conceive some genius will some day present it—with brilliant simplicity and, withal, rigidly.

To those who, in philosophic mood, would question what I mean by simplicity and rigidity I will answer that the pronouncements of genius determine this, that we recognize it when it comes and dream of it before it comes. And come it must if those who labor with life chemistry are ever to apply effectively all the pertinent information being gathered, often with lack of systematic thoroughness and being recorded with ever increasing inavailability.

In undertaking the difficult task of revision I have sought and have been generously given the aid of many friends and authorities. Since none of these has seen the manuscript in final form I shall not note the subjects on which advice was given, lest, perchance, the mishandling of the advice reflect upon the giver. I hope that this will not seem to detract from the gratitude I have or from the credit due to:

Mr. C. E. Abromavich   Dr. Lloyd Felton
Mr. Alan Bernstein   Dr. F. Fenwick
Dr. William Blum   Dr. H. D. Gibbs
Dr. Barnett Cohen   Dr. A. Grollman
Dr. N. Ernest Dorsey   Dr. Louis J. Gillespie

Poincaré in *The Foundations of Science* remarks, "There are facts common to several sciences, which seem the common source of streams diverging in all directions and which are comparable to that knoll of Saint Gothard whence spring waters which fertilize four different valleys."

Such are the essential facts of electrolytic dissociation.

Among the numerous developments of the theory announced by Arrhenius in 1887 none is of more general practical importance than the resolution of "acidity" into two components—the concentration of the hydrogen ions, and the quantity of acid capable of furnishing this ionized hydrogen. For two reasons the hydrogen ion occupies a unique place in the esteem of students of ionization. First, it is a dissociation product of the great majority of compounds of biochemical importance. Second, it is the ion for which methods of determination have been best developed. Its importance and its mensurability have thus conspired to make it a center of interest. The consequent grouping of phenomena about the activity of the hydrogen ion is unfortunate when it confers undue weight upon a subordinate aspect of a problem or when it tends to obscure possibilities of broader generalization. Nevertheless, such grouping is often convenient, often of immediate value and frequently illuminating. Especially in the field of biochemistry it has coördinated a vast amount of material. It has placed us at a point of vantage from which we must look with admiration upon the intuition of men like Pasteur, who, without the aid of the precise conceptions which guide us, handled "acidity" with so few mistakes.

In the charming descriptions of his experimental work Pasteur has given us glimpses of his discernment of some of the effects of "acidity" in biochemical processes. In the opening chapter of *Studies on Fermentation* he noted that the relatively high acidity of must favors a natural alcoholic fermentation in wine, while the low acidity of wort induces difficulties in the brewing of beer. He recognized the importance of acidity for the cultivation of

the bacteria which he discovered and was quick to see the lack of such an appreciation in his opponents. In describing that process which has come to bear his name Pasteur remarks, "It is easy to show that these differences in temperature which are required to secure organic liquids from ultimate change depend exclusively upon the state of the liquids, their nature and above all upon the conditions which affect their *neutrality whether towards acids or bases.*" The italics, which are ours, emphasize language which indicates that Pasteur was aware of difficulties which were not removed till recently. Had Pasteur, and doubtless others of like discernment, relied exclusively upon volumetric determination of acidity they would certainly have fallen into the pitfalls which at a later date injured the faith of the bacteriologist in the methods of the chemist. Was it reliance upon litmus which aided him? Perhaps the time factor involved in the use of litmus *paper*, which is now held as a grave objection, enabled Pasteur to judge between extremes of reaction which the range of litmus as an indicator in equilibrium does not cover. At all events he recognized distinctions which we now attribute to hydrogen ion concentrations. Over half a century later we find some of Pasteur's suggestions correlated with a marvelous development in biochemistry. The strongest stimulus to this development can doubtless be traced to the work of Sørensen at the Carlsberg Laboratory in Copenhagen and not so much to his admirable exposition of the effect of the hydrogen ion upon the activity of enzymes as to his development of methods. At about the same time Henderson of Harvard, by setting forth clearly the equilibria among the acids and bases of the blood, indicated what could be done in the realm of physiology and stimulated those researches which have become one of the most beautiful chapters in this science.

Today we find new indicators or improved hydrogen electrode methods in the physiological laboratory, in the media room of the bacteriologist, serving the analyst in niceties of separation and the manufacturer in the control of processes. The material which was admirably summarized by Michaelis in 1914, and to which Michaelis himself had contributed very extensively, presents a picture whose significance he who runs may read. There is a vast field of usefulness for methods of determining the hydro-

gen ion. There is real significance in the fruits so far won. There remain many territories to explore and to cultivate. We are only at the frontier.

In the meantime it will not be forgotten that our knowledge of the hydrogen ion is an integral part of a conception which has been under academic study for many years and that the time has come when the limitations as well as certain defects are plainly apparent. While there is now no tendency nor any good ground to discredit the theory of electrolytic dissociation in its essential aspects, there is dissatisfaction with some of the quantitative relationships and a demand for broader conceptions. It requires no divination to perceive that while we remain without a clear conception of why an electrolyte should in the first instance dissociate, we have not reached a generalization which can cover all the points now in doubt. Perhaps the new developments in physics will furnish the key. When and how the door will open cannot be foreseen; but it is well to be aware of the imminence of new developments that we may keep our data as pure as is convenient and emphasize the experimental material of permanent value. We may look forward to continued accumulation of important data under the guidance of present conceptions, to distinguished services which these conceptions can render to various sciences and to the critical examination of the material gathered under the present régime for the elements of permanent value. These elements will be found in the data of direct experimentation, in those incontrovertible measurements which, though they be but approximations, have immediate pragmatic value and promise to furnish the bone and sinew of future theory. In the gathering of such data guiding hypotheses and coördinating theories are necessary but experimental methods are vital.

The time seems to have come when little of importance is to be accomplished by assembling under one title the details of the manifold applications of hydrogen electrode and indicator methods. It would be pleasing to have in English a work comparable in scope with Michaelis' *Die Wasserstoffionenkonzentration;* but even in the short years since the publication of this monograph the developments in special subjects have reached such detail that they must be redispersed among the several sciences, and made an integral part of these rather than an unco-

ordinated treatise by themselves. There remains the need for a detailed exposition, under one cover, of the two *methods* which are in use daily by workers in several distinct branches of biological science. It is not because the author feels especially qualified to make such an exposition that this book is written, but rather because, after waiting in vain for such a book to appear, he has responded sympathetically to appeals, knowing full well from his own experience how widely scattered is the information under daily requisition by scores of fellow workers.

For the benefit of those to whom the subject may be new there is given in the last chapter a running summary of some of the principal applications of the methods. This is written in the form of an index to the bibliography, a bibliography which is admittedly incomplete for several topics and unbalanced in others, but which, it is believed, contains numerous nuclei for the assembling of literature on various topics.

The author welcomes this opportunity to express his appreciation of the broad policy of research established in the Dairy Division Laboratories of the Department of Agriculture under the immediate administration of Mr. Rawl and Mr. Rogers. Their kindness and encouragement have made possible studies which extend beyond the range of the specialized problems to which research might have been confined and it is hoped that the bread upon the waters may return. To Dr. H. A. Lubs is due the credit for studies on the synthesis of sulfonphthalein indicators which made possible their immediate application in bacteriological researches which have emanated from this laboratory. Acknowledgment is hereby made of the free use of quotations taken from the paper *The Colorimetric Determination of Hydrogen Ion Concentration and Its Applications in Bacteriology* published in the *Journal of Bacteriology* under the joint authorship of Clark and Lubs.

The author thanks his wife, his mother, Dr. H. W. Fowle and Dr. H. Connet for aid in the correction of manuscript and proof, and Dr. Paul Klopsteg for valuable suggestions.

It is a pleasure to know that the publication of the photograph of Professor S. P. L. Sørensen of the Carlsberg Laboratory in Copenhagen will be welcomed by American biochemists all of whom admire his work.

Chevy Chase, Maryland
March 17, 1920

CHAPTER I

INTRODUCTION

AND

THE SIMPLER EQUILIBRIUM EQUATIONS FOR ACIDS AND BASES

*In a country rich in gold observant wayfarers may find nuggets on
their path, but only systematic mining can provide the currency
of nations.*—SIR FREDERICK HOPKINS.

INTRODUCTION

"Acid" still means sour, like vinegar. This common meaning
preserves the ancient flavor of the word and recalls the fact that
the modern highly technical meaning had its origin in the grouping
of substances by type. In this there is a resemblance to the pro-
cedure of the botanist who in the last analysis determines a
species by reference to a type specimen. But once we pass beyond
the mere origin of the modern meaning we may trace persistent
searches among the sour or vinegar-like substances for the nature
of that community of properties which came to be regarded as of
much more fundamental interest than the classification itself.
Each attempt bears the imprint of its age. By Paracelsus the
community of properties was supposed to reside in the *Acidum
primogenium*. By Lavoisier, the discoverer of the true nature of
oxygen, it was associated with oxygen. Mills, in philosophic
mood, called it a function. In the age of structural and atomic
chemistry it was hydrogen so placed in a compound as to be
replaceable by a metal. Fortunately no categorical distinction
between property, function, substance, etc., deterred the searchers.

Among the properties common to the sour or acid substances
is their submission to the "killing"[1] effect of alkalies. "Alkali"

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[1] The word "kill," taken from the vernacular discussion of the phenom-
enon in question, is much more appropriate to this stage of the discussion
than certain other words like "neutralize" which, in the parlance of the
laboratory, have acquired meanings so specialized and at the same time so
diverse as to obscure meaning very successfully.

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is said to originate in an Arabic word meaning the ashes of plants. From this origin has arisen a variety of meanings illustrating admirably another search for an account of another community of properties. From wood ashes has been isolated potassium, a metal having properties in common with lithium, sodium, etc. This series is now known as that of the "alkali metals." To a certain degree their properties extend to the group of metals known as the "alkaline earths." Metals of either group act vigorously upon water and the resulting solutions have preeminently a property in common with the leachings of wood ashes. They "kill" the acidity of acid solutions. They are "alkaline."

An alkali upon interacting with an acid forms a salt, for example caustic potash and hydrochloric acid form the salt potassium chloride. In a chemistry which elevated the importance of the metals, the potassium in potassium chloride held the center of interest. It was considered the *base* of the salt. But "base" in this sense is going out of common usage. Again a property, the basic property, has been abstracted and "base" is now the preferred word with which to denote all substances, organic as well as inorganic, which act like the leachings of wood ashes in killing acids.

There are many evidences of the mutual destruction (complete or partial) of properties of the two groups, when acids and bases interact. Attempts to systematize these evidences have had their important part in developing a classification of specific substances into acidic and basic compounds. Some of the systems of classification have extended far beyond the bounds of their concrete origin. We need not recreate for ourselves the perplexities which arose during attempts to make the classification of acids and bases scientifically definite. But in passing we may recall that the older theories were reduced by the "practical" chemist to meet his demand that an acid solution turn litmus red and an alkaline solution turn litmus blue. The ghost of this delightfully simple basis still lingers about the laboratory, although the litmus test is now recognized as hopelessly inadequate for analysis, for organic synthesis, for biochemistry, and for a host of industrial processes. If we ignore the older classifications, it is not because there is any occasion to disclaim our debt to the early investigators. They provided the foundations of our far-reaching

subject. From these foundations have arisen some concepts and some specific data of such importance as to merit our entire attention. The purely historical we shall leave to the historian.

We need only note that the process of abstraction has progressed until a property common to wood ashes, alkali carbonates, hydroxides in general and a host of organic compounds has been elevated to unique distinction. A similar abstraction has occurred in the treatment of acids; and at last we associate properties with material entities again. The entities appear in the following definitions, and their associations with properties appear in those manifold consequences which will be touched upon throughout this book.

For present purposes we may define an acid as any substance which is capable of supplying to its solution, or to another substance, hydrogen bearing a positive electric charge. An instance is hydrogen chloride, HCl, which splits to form H^+ and Cl^-.

Likewise we may define a base as any substance which is capable of supplying to its solution or to another substance the electronegative group OH^-. An instance is sodium hydroxide, NaOH, which splits to form Na^+ and OH^-.

Like the Greeks who personified the virtues, we, having embodied the acidic and the basic properties, have lifted to our Olympus the hydrogen and the hydroxyl ions, H^+ and OH^-. Furthermore the current conception of the nature of acids and bases bears the imprint of the age of electricity.

Having touched upon the electrical aspect we might be tempted to carry the theme forward into the whirl of current concepts regarding the electrical nature of matter. Some of these concepts will be used in later chapters; but, for the most part, they will not be essential to our present theme. Without necessarily losing sight of adjacent subjects, we may, (as we are entitled to do) establish a province for our own subject. We may draw from the adjacent subject helpful pictures; but as our theme progresses it will be perceived that our task is to formulate a set of phenomena, that the *organization* of the material within the chosen province is our subject and that any reconstruction of the physical meaning of the terms will affect but little the essential *organization* with which we are concerned.

All too briefly we shall touch first upon the adjacent subject.

According to current conceptions, the atom of hydrogen, the simplest of the chemical elements, concentrates the greater part of its mass in a nucleus having unit, positive, electrical charge. (See figure 1, a.) Frequently this nucleus is called the proton. About this rotates an electron, the unit, negative, electric charge. This apposition of the unit charges of opposite sign renders the atom as a whole electrically neutral.
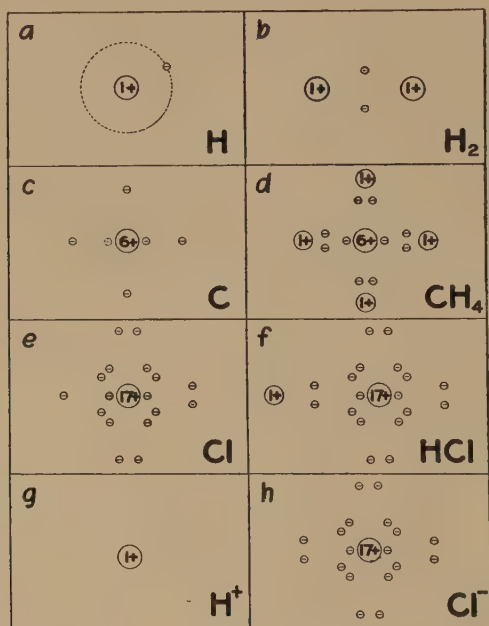
FIG. 1. SCHEMATA OF ELEMENTS, MOLECULES AND IONS

Nuclei with + charges; electrons with − charges. *a*, hydrogen atom; *b*, hydrogen molecule; *c*, carbon atom; *d*, methane molecule; *e*, chlorine atom; *f*, hydrogen chloride molecule; *g*, hydrogen ion; *h*, chloride ion.

Atoms of other elements are built of nuclei having several excess positive electrical charges and of extra-nuclear, planet-like electrons, the total number of which in the electrically neutral atom must be equal to the net, nuclear, positive charge. (See figure 1, c and e.) This number is the so-called atomic number of the element. For example the atomic number of carbon is 6 and of chlorine 17.

It is profitable to assume that the essential, structural aspect of compound formation is a sharing of the outer electron orbits

of the component atoms such that not only is the compound as a whole electrically neutral but that an element such as carbon or chlorine completes a stable octet of electrons in its outer shell. Thus the structure of methane is suggested by the formalistic, static diagram in one plane shown in figure 1, d. Since the outer electron orbits are considered all-important in the formation of such compounds, all parts of carbon except the outer electrons can be represented by C, atomic carbon itself by $\cdot \overset{\cdot}{\underset{\cdot}{C}} \cdot$ and methane,

for example, by $H : \overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{C}} : H.$ Likewise hydrochloric acid is repre-

sented by $: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : H,$ and the chlorine molecule by $: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} :.$ The hydrogen molecule, being stable with a pair of electrons shared by the two protons, is represented by $H : H.$ The hydrogen ion appears as a proton stripped of electrons.

Physical theory demands rotation of the planet-like electrons, while chemical theory demands some sort of resultant effect which will account both for the positions of elements relative to one another when in chemical combination and for that curiously vague yet definite something called valence. Pending the results of attempts to meet both demands, it has become the custom to picture the spatial and valence aspect by representations such as those of figure 1 or their abbreviations given above; but it should be remembered that the apparently implied static positions of the electrons merely represent effects which come within the range of elementary chemical demands.

The picture given above and in figure 1 will be found elaborated upon in *Valence* by G. N. Lewis, 1923. It is critically discussed by Andrade (1927) in whose popular book *The Structure of the Atom* will be found references to the more important papers on the subject. The chief success of the theory in the field with which we are concerned has been an attractive, orderly redescription of well known fact with a few predictions of minor importance. The student should be very careful to use the picture as a convenience, subject to radical change if required when the gap between the demands of chemistry and physics is bridged.

In some of the compounds of hydrogen the sharing of electrons may be so complete as to make difficult the detachment of the hydrogen nucleus; in other compounds the electron of the hydrogen atom may occasionally be captured and the proton be left free to escape; in some cases the capture may be complete and

decisive. In the last case it would appear that only the electro-static attraction of the oppositely charged parts might keep the compound intact and that an environment tending for any reason to favor dispersion would favor complete dissociation. Thus the dissociation of HCl (fig. 1, f) would furnish H^+ (fig. 1, g) and Cl^- (fig. 1, h) in high degree.

Whether all or only a very few of the hydrogen nuclei (protons) in a mass of a given compound escape, those which do escape act as discrete entities contributing their part to the osmotic pressure of a solution and to all the other so-called colligative (bound together) properties of a solution such as the lowering of the freezing point, rise in the boiling point, etc. These effects are discussed in all texts of physical chemistry and need not be reviewed here. In aqueous solution the escaped hydrogen nucleus may combine with water molecules; but the charge is preserved. Therefore, under the stress of an electric field, the particle will travel toward the cathode.[2] Hence it is called an *ion* (traveler), more specifi-cally a *cation*, and quite specifically it is called the *hydrogen ion* or *hydrion*.[3]

In cases rarely encountered, for instance in the compound LiH, the hydrogen nucleus not only tends to hold its own electron but may take the lithium valence electron from the environment of the lithium nucleus. On dissociation of this compound there is formed the negative hydrogen ion.[4] In gaseous form molecules of hydrogen (H_2) may become charged and thus become gaseous ions. Neither of these two types is to be considered. It will be under-stood that the term hydrogen ion or hydrion as used in this text refers to the species H^+. When using this symbol we ignore the water of hydration. (See page 540.)

It is suspected that the development of this subject may show

[2] Frequently there will be occasion to introduce a technical term the meaning of which is understood by the majority of readers. To interrupt the exposition by introducing definitions of all the technical terms which will be used would not be practical. It might prove distracting to the novice and irritating to the more advanced student. As an imperfect compromise there are assembled in appendix N definitions of the more im-portant technical terms used in this book and not defined in the text.

[3] The two terms will be used without discrimination in order to make the reader familiar with each as they occur in current literature.

[4] See Klemenc (1921) on negative hydrion.

that such a readily dissociable compound as hydrogen chloride has a structure radically distinct in type from that of so stable a compound as methane. The latter must suffer drastic treatment before it yields evidence of dissociation. Nevertheless the tendency of compounds to throw off or surrender hydrions, as measured in terms presently to be described, grades without any serious discontinuity[5] from that high degree displayed by hydrogen chloride, through the comparatively weak yet very distinct tendencies displayed by many carboxylated compounds (*e.g.*, acetic acid), on to the barely measurable tendencies in certain alcohols. Even beyond the measurable lie cases for which the presumption of ionizable hydrogen is often useful.

In dealing with these matters we shall find ourselves fully occupied with the laws governing dissociation in mass and we shall not be concerned with the architecture and the electronic structure of the individual molecule. We must circumscribe our subject matter and we may begin its exposition either with the acceptance of the evidences for ionization or by introducing the fundamental concepts as pure postulates. Indeed it is significant that many modern authors go to no trouble to justify these concepts before introducing them in a manner which would lead the logician to the conclusion that they are pure postulates. The reason is simple. The best evidences of the realities to be considered are found in those *quantitative* relations which can hardly be appreciated before the method of formulation is developed.

Let it be said here most emphatically that our first formulation will be as a map drawn for a locality. If extended far it will need to be drawn with additional devices comparable with Mercator's projection for the use of navigators. Like the map of a locality, our map is good for restricted conditions. Like the projection of Mercator, the corrected map is good for distant voyages even if it distort reality. It is of more importance to indicate how certain experimental devices yield results which appear to be in substantial agreement locally and in conflict extralocally. This is because these devices operate in ways as distinctly different as the sextant and the compass. Surveys

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[5] There have been several expressions of the opinion that a statistical study would show a more or less distinct "break" between the frequencies of occurrence of "strong" and "weak" acids.

by sextant or compass can be made from the same base line; and either map, without correction to the terms of the other, is valid locally. Difficulties arise if the distinctly different natures of the two methods are not recognized when the traveler is on distant voyages, or in the presence of local perturbations.

THE CONCEPT OF EQUILIBRIUM

Reversibility

Imagine an acid of the type HA dissociating into the cation H^+ and the anion A^-.

$$HA \rightleftharpoons H^+ + A^- \tag{1}$$

Arrows in place of an equation sign were introduced by van't Hoff to indicate not only the equivalence expressed by the usual equation sign but *reversibility*. In other words there occur among the large number of anions and cations, present in any ordinary aqueous solution of the acid, recombinations of the ions the while some of the HA molecules are dissociating.

This conception of a "reaction" as labile, continuous and reversible is of profound importance. So long as analysts are content to balance the two sides of such a written form for the purpose of expressing stoichiometrical relations of ordinary analytical importance the equation sign suffices and the implications symbolized by the arrows may be neglected. But as a matter of fact it is of particular importance to analysis to regard reactions as not necessarily going to completion in one direction. The concept of reversibility[6] is particularly applicable to the ionization of acids and bases and to many reactions in which acids and bases take part. So, in terms of reversible reactions, the geologist describes the laying of the limestone stratum and the return of the "everlasting hills" to the "eternal drift."

Our modern views of chemical reversibility supplement the ancient views of mechanical reversibility which Mallock[7] has paraphrased.

[6] This is not to be confused with reversibility in a strict thermodynamic sense.

[7] Mallock, *Lucretius on Life and Death*.

No single thing abides, but all things flow,
Fragment to fragment clings; the things thus grow
        Until we know and name them.   By degrees
They melt, and are no more the things we know.
. . . .
Nothing abides.   Thy seas in delicate haze
Go off; those moonéd sands forsake their place;
        And where they are shall other seas in turn
Mow with their scythes of whiteness other bays.

As if playing a joke on Fate, Life seems to have seized upon
delicate balances in just such processes as determine the destiny
of mountains and, unlike the Inanimate, has made these balances
the internal environment of its potentially immortal cells.

In the ceaseless interplay of the components of a given, re-
versible reaction, the following situation may occur.   The reac-
tion may proceed no faster in one direction than in the other.   An
indication of this state is the absence of change in the quantities
of the components of the system.   Statistically the system is at
rest.   This is the state of equilibrium.

THE EQUILIBRIUM EQUATION FOR ACID DISSOCIATION

At the start let there be no attempt to describe all the factors
which increasingly refined technique forces into view.   Let there
be imagined an ideally simple system in which each component
represented in equation (1), while free, behaves as if it were un-
affected by the presence of the other solutes.   Let a variation of
the concentration of any component not affect the imagined
constancy of the environment.

Let brackets about a symbol indicate concentration of the
species which the symbol represents and let concentration be ex-
pressed in moles per liter of solution.   Thus [HA] represents x
moles of residual undissociated acid, HA, per liter.

We need not enquire concerning the forces or the circumstances
which occasion the ionization of the individual, acid molecule.
We need only assume that occasionally the molecule acquires the
ability to ionize and does ionize.   Then, since enormous numbers
of molecules are present in solutions even of high dilution, we
may treat the subject in a crude, statistical way and imagine that
each molecule has, on the statistical average, the same span of

life. Then the velocity, v_1, with which the concentration of HA is decreasing *at any instant*, is proportional to the concentration [HA] *at that instant.*

$$v_1 = k_1[HA] \qquad (2)$$

In (2) k_1 is a proportionality factor. Its value, as we shall see presently, need not be determinable.

The velocity of the reverse reaction, wherein ions combine to reconstruct HA, is likewise dependent on the concentrations [H$^+$] and [A$^-$] and in the following manner.

Suppose, to begin with, that there were equal numbers of hydrions and anions. Then imagine that the number of hydrions in a given volume were tripled. The number of collisions between hydrions and anions would be tripled. If the original number of hydrions remained and the number of anions were tripled the number of collisions would be tripled. But if the hydrions were tripled and the anions were tripled simultaneously, the number of collisions would be nine times the original. Thus the number of collisions is *proportional to the product of the concentrations.* Combination may not necessarily be determined by collision alone. A favorable orientation during collision may be necessary. A heightened energy may be necessary. But, if we idealize the situation, we may suppose that successful combination is that constant fraction of collisions which is determined by a particular environment and by the specific natures of the ions concerned. Then in equation (3) the proportionality factor k_2 expresses not only proportionality of combination to collisions but proportionality to other factors which are idealized as constant.

We have then for the velocity of combination

$$v_2 = k_2 \, [A^-] \, [H^+] \qquad (3)$$

Having already defined the state of equilibrium as that at which the velocity of change in one direction equals the velocity in the opposite direction, we let v_1 and v_2 be *those* velocities which occur *at* the attainment of equilibrium and accordingly we equate the two. Whence from (2) and (3) there is obtained (4).

$$\frac{[A^-]\,[H^+]}{[HA]} = \frac{k_1}{k_2} = K_a \qquad (4)$$

For the ratio of two constants in (4) there is substituted the one constant K_a, which is properly called the equilibrium constant. It will be noted that the ion concentrations are placed in the numerator of (4). Had they been placed in the denominator the equilibrium constant would be the reciprocal of K_a. When the *convention* used in (4) is followed, the constant (*i.e.*, K_a) is called the dissociation constant. Its reciprocal, $\frac{1}{K_a}$, is called the association constant.

The dissociation constant is sometimes described as a measure of the "strength" of an acid. Thus the following comparison may be made.

CLASS	COMPOUND	K_2 (APPROXIMATE)
Strong acid................	HCl	About 10^{+7}
Moderately strong acid.........	Dichlor acetic acid	About $5. \times 10^{-2}$
Weak acid....................	Acetic acid	1.8×10^{-5}
Very weak acid...............	Phenol	1.0×10^{-10}
Extremely weak acid..........	Glucose	4×10^{-13}
Vanishingly weak acid.........	Methane	Approaches 0

For tables of dissociation constants see appendix tables G, H, I, and J.

To indicate that a dissociation constant, as used in these approximate equations, applies to a limited set of conditions, it is frequently written K'. K is then reserved for the "true" dissociation constant, which can be estimated by the method of Chapter XXV.

It is readily perceived that, when actual numerical values are given to the concentrations of the several "species" occurring in the equilibrium equation, care must be taken to use a consistent unit of concentration. If grams per liter in one case, moles per liter of solution in another, moles per 1000 grams of solvent in another and millimoles per liter of solution in another case were used, the equilibrium constants, while well defined in each case separately, would not be comparable.

Of course, if there be reason to believe that an acid like HCl, or a salt like NaCl, is ionized *almost completely* in dilute solutions, there is little point in attempts to apply *to experiment* the treatment which follows the

derivation given. As noted later, the application of the type equilibrium equation to a case like

$$\frac{[Na^+]\ [Cl^-]}{[NaCl]} = K \quad \text{or} \quad \frac{[H^+]\ [Cl^-]}{[HCl]} = K_a$$

has no practical value. In the first place, if the quantity in the denominator of the type equation should approach an infinitesimal, the most extreme accuracy would be required to satisfy the equation experimentally. Furthermore the simple equation is founded upon an idealization, and in the case specified the utmost accuracy would be required to detect and to measure the several factors which might interfere with the applicability of the ideal equation. But, in the second place, the introduction of a concentration of a molecule like NaCl or HCl would be to confess one's ignorance of the fact that the evidence is against the existence of the *molecule* NaCl and (for aqueous solutions) against the existence of the *molecule* HCl. (See page 58.) A dilute solution of hydrochloric acid may be regarded as one extreme. A solution of methane is a case at the other extreme. In the first case K_a approaches infinity; in the second K_a approaches zero. In either circumstance the type equation has little practical value.

APPLICATION TO A SIMPLE ACID SOLUTION

Since the concentrations of the various "species" are treated like the x, y, z of any ordinary algebraic equation, it may be interesting to note at this point a special application of equation (4) which will involve some simple algebra.

Consider a solution containing the acid as the only solute and neglect the ions which may come from water. The simple acid HA *partially* dissociates into equal parts of H^+ and A^-. Hence

$$[H^+] = [A^-]$$

Let the concentration of total acid [S] be defined by

$$[S] = [HA] + [A^-],$$

i.e., the sum of the concentrations of undissociated and dissociated acid. Equation (4) may now be written as follows

$$\frac{[H^+]^2}{[S] - [H^+]} = K_a \qquad (5)$$

Equation (5) may be solved for $[H^+]$ by the usual process of "completing a square." There is thus obtained

$$[H^+] = \sqrt{K_a\ [S] + \frac{K_a^2}{4}} - \frac{K_a}{2} \qquad (6)$$

When K_a is small in relation to $[S]$

$$[H^+] \cong \sqrt{K_a\,[S]} \tag{7}$$

Example: Given $K_a = 1 \times 10^{-5}$; calculate $[H^+]$ when $[S] = 0.1$ molar.

$$[H^+] = \sqrt{(10^{-5})\,(10^{-1}) + \frac{10^{-10}}{4}} - \frac{10^{-5}}{2}$$

Approximately:

$$[H^+] = \sqrt{10^{-6}} = 10^{-3} = 0.001 \text{ normal}$$

Application of (6) to the case of the acid having the value 10^{-5} for K_a will show that the approximation of (7) introduces a significant error when $[S]$ is less than 0.001 normal. For dilute solutions and for solutions of very weak acids, account must be taken of the hydrions coming from the water as will appear presently.

GENERAL EXTENSION OF THE EQUILIBRIUM EQUATION TO MIXTURES

When an anion originates by the dissociation of the acid HA or by the dissociation of some admixed salt, such as NaA, it may combine with any hydrion irrespective of the source of this hydrion. Therefore equation (4) holds even in mixtures,—with the qualification that the actual value of K_a may vary somewhat even in solutions of the same solvent and of the same temperature, if the components of the system vary sufficiently in concentration to alter appreciably the environment. This, in our idealization, we demanded should be constant.

To embrace the situation to be considered when salts of the acid are present, let $[S]$, the concentration of total material containing the acid's main group in the form of ions or ionogens, be defined by

$$[S] = [A^-] + [HA] + [s] \tag{8}$$

Here $[s]$ represents the sum of the concentrations of all those *salts* of the acid which are in an *undissociated* state.

Equations (4) and (8) yield (9)[8]

$$\frac{[A^-]}{[S]} = \frac{K_a}{K_a + [H^+]}\left(1 - \frac{[s]}{[S]}\right) \tag{9}$$

It can be said at once that if (9) be applied to experimental data it will appear as if [s] should be considered a variable of significant magnitude. On the other hand there are frequently good reasons for believing a salt to be practically completely ionized and in these cases it is permissible to let [s] = 0. Indeed, effects which might be attributable to the formation of undissociated salt molecules are now attributed to the attraction between its charged ions and are dealt with by the special methods of Chapter XXV.

It should not be assumed that there are no cases in which there is undissociated salt. However, we shall continue as if for cases in which it can be assumed that the concentration of undissociated salt is so small as to be negligible. Then [s] in equation (9) is considered zero and (9) reduces to (10)

$$\frac{[A^-]}{[S]} = \frac{K_a}{K_a + [H^+]} \tag{10}$$

In either case the ratio $\dfrac{[A^-]}{[S]}$ is called the fraction of dissociation or degree of dissociation. This refers not to the acid alone but to all the ionogens capable of supplying to the solution the specific ion A^-. This ratio is so frequently used that it is a convenience to give it the symbol α. Percentage dissociation $= 100\alpha$.

Then (10) is written:

$$\alpha = \frac{K_a}{K_a + [H^+]} \tag{10a}$$

Equation (10a) emphasizes, in a very direct way, the fact that changes in the hydrion concentration of a solution indicate alteration of α, the degree of dissociation,—that is, the degree to which the specific acid under consideration is present in the dissociated state. This is the key equation unlocking the door to most of the reasons for interest in methods of determining hydrion concentrations. For, since $[H^+]$ indicates α in a specific case, $[H^+]$

---

[8] Since the term $(1 - \frac{[s]}{[S]})$ in (9) is to be eliminated the student is advised to develop the simpler equation (10) by neglecting [s] in equation (8).

indicates the *degree* to which properties associated with the anion or properties associated with the undissociated residue will be manifest *in mass*.

This simple equation sums up the main feature of most that follows. However, it is more convenient in logarithmic form.

LOGARITHMIC FORMS OF THE FUNDAMENTAL EQUATIONS

Because the values of $[H^+]$ may vary so greatly that charting on a linear scale is impracticable and because of other better reasons, it is both convenient and logical to use a logarithmic function of $[H^+]$. That chosen is $\log_{10} \dfrac{1}{[H^+]}$. To this is given the symbol pH (see page 36).

For the sake of simplicity continue with the assumption that $[s]$ in equation (9) is so small that it may be considered zero. Equation (10a) is then applicable and may be transformed to (11)

$$[H^+] = K_a \frac{1 - \alpha}{\alpha} \tag{11}$$

Taking the logarithm of the reciprocal of each side of (11) we have (12) which is merely another form of the key equation (10a) and is the most generally useful of all the equations with which we shall deal. The greater part of the subject can be developed with the aid of this equation.

$$pH = \log \frac{1}{[H^+]} = \log \frac{1}{K_a} + \log \frac{\alpha}{1 - \alpha} \tag{12}$$

Analogous to the expression $pH \equiv \log \dfrac{1}{[H^+]}$ is the expression $pK_a \equiv \log \dfrac{1}{K_a}$. Since the current literature cannot be understood without an appreciation of the meaning of pK_a[9] we shall not hesitate to adopt this symbol. Then (12) may be written:

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha} \tag{12a}[10]$$

[9] Bjerrum (1923) calls pK_a the dissociation exponent.
[10] This is the most important equation of the book. The student is advised to calculate pH with any given value of pK_a and values of α ranging from 0.1 to 0.9 at intervals of 0.1, and to chart the results as in figure 2.

It will be remembered that α is the degree of dissociation. If we can assume that a mixture of equivalents of acid and base forms a salt which dissociates completely, α should be 1 for such a mixture. If the acid is so very weak that its dissociation is negligible compared with that of the salt, we can assume (as an approximation) that α is approximately the same as the corresponding degree of "neutralization"[11] i.e., salt formation. In
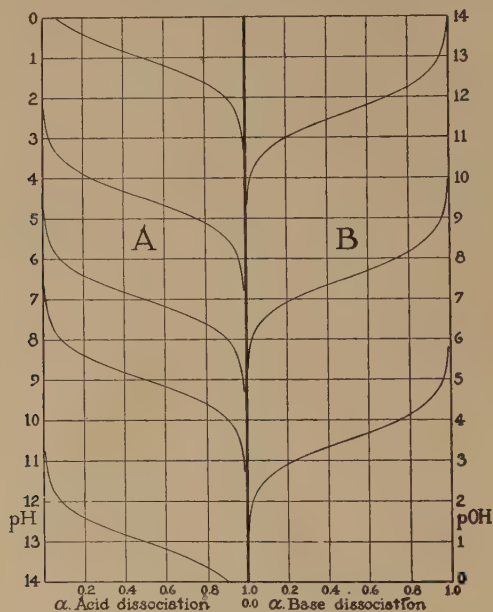
FIG. 2. (A) RELATION BETWEEN pH AND THE DEGREE, α, OF THE DISSOCIATION OF ACIDS; (B) RELATION BETWEEN pH AND THE DEGREE, α, OF THE DISSOCIATION OF BASES

other words the curve relating α to pH may, under the specified conditions, be closely comparable with the curve relating degree of neutralization to pH. Equation (12a) may then be written in *approximate* form as:

$$pH = pK_a + \log \frac{[salt]}{[acid]} \tag{12b}$$

This equation will be derived again later.

[11] "Neutralization" is here used in the loose sense that each equivalent of base destroys the acidic nature of one equivalent of acid.

The geometry corresponding to equation (12) or (12a) is shown by figure 2 A. All the curves are identical in form. The position of any one is determined by the value of pK_a, for, since $[H^+] = K_a$ when $\alpha = 0.5$, the midpoint of the curve is determined by pK_a.

BASES

Before dwelling more at length upon equation (12) and upon the corresponding geometry, there will be considered the fundamental equation for the equilibrium state in the dissociation of a base.

It has been customary to regard oxides such as K_2O, which on solution in water give tests for alkalinity, as if they became hydrated to compounds of the type BOH (e.g., $K_2O + H_2O \rightarrow 2KOH$). The alkalinity of the solution is then assumed to be due to the ionization of BOH to furnish some definite concentration of the hydroxyl ion, OH^-.

For the reversible reaction:

$$BOH \rightleftharpoons B^+ + OH^-$$

there may be written the equilibrium equation:

$$\frac{[B^+][OH^-]}{[BOH]} = K_b \qquad (13)$$

Equation (13) is to be regarded as the type equation. It is not applied in practice to a base such as KOH which is practically completely dissociated in dilute solution. Such a case is best treated in another manner. (Compare page 12.)

Applying to (13) the same sort of mathematical treatment accorded (4) we reach in turn (14), (15), and (15a).

$$\alpha = \frac{K_b}{K_b + [OH^-]} \qquad (14)$$

$$pOH = \log \frac{1}{[OH^-]} = \log \frac{1}{K_b} + \log \frac{\alpha}{1-\alpha} \qquad (15)$$

$$pOH = pK_b + \log \frac{\alpha}{1-\alpha} \qquad (15a)$$

In the latter cases pOH symbolizes $\log \dfrac{1}{[\text{OH}^-]}$ and $pK_b \equiv \log \dfrac{1}{K_b}$.

The geometry of (15a) is illustrated by the curves of figure 2 B. Again this equation gives a family of curves. Any one curve is fixed in its position by the value of pK_b.

For a reason presently to become clear, values of pOH in figure 2 B are plotted in a direction opposite to the direction of increasing values of pH.

THE WATER EQUILIBRIUM

Up to this point no relation has been shown between the acid systems and the base systems nor between pH and pOH. If we confine our attention to aqueous solutions we may now introduce the fact that water yields both hydrions and hydroxyl ions in accordance with

$$\text{HOH} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

For the equilibrium state of this reaction write:

$$\frac{[\text{H}^+]\,[\text{OH}^-]}{[\text{HOH}]} = k$$

Anticipating a conclusion to be mentioned in Chapter II, we may state that water is so little dissociated that no serious error will be made in regarding the concentration of the undissociated residue, [HOH], to be equal to that of the total water. Furthermore this may be considered constant for limited ranges of dilute solutions. Hence:

$$[\text{H}^+]\,[\text{OH}^-] = K_w \tag{16}$$

Properly K_w is an ionic product, but it is commonly called the dissociation constant of water. Like all the other so-called equilibrium constants, it is only a constant by grace of the maintenance of a constant environment. Its value is subject to change with change of temperature, salt concentration, etc. For descriptive purposes K_w may be considered to have the rounded value 10^{-14}.

From (16) there is readily derived the following;

$$\log \frac{1}{[H^+]} + \log \frac{1}{[OH^-]} = \log \frac{1}{K_w}$$

$$pH + pOH = pK_w \tag{17}$$

and, since the value of K_w may be rounded off to 10^{-14},

$$pH + pOH = 14 \tag{17a}$$

It is this relation which was used in aligning the pH and pOH values of figure 2.

MORE DETAILED EQUATIONS

It is unnecessary for purposes of general treatment to develop separate equations for acid systems and for base systems. This will be shown in Chapter II. Therefore, we shall confine attention to the equations for acid systems in a discussion of more detailed equations.

In considering the following treatment the student is advised to pay little attention to the mathematical derivations of equation (19) or (20). They are stated in their elaborate form for convenience of discussion. In this discussion there will be shown, by one numerical example, conditions under which certain of the quantities as they occur in the equation can be neglected. This will aid in the justification of the useful approximation to follow in the next section.

In the derivation of equation (12) there were introduced—in addition to the idealistic assumptions at the very origin—two approximations. One, the neglect of the undissociated salt [s], we have already mentioned. The other was the neglect of the hydrions and hydroxyl ions coming from the solvent, water.

In addition to the familiar equation

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a$$

and the summation (8) which is

$$[S] = [A^-] + [HA] + [s]$$

it now becomes necessary to employ equation (18) which will automatically take account of the hydroxyl and hydrions arising from the water.

$$[H^+] + [B^+] = [A^-] + [OH^-] \qquad (18)$$

This new equation expresses the electro-neutrality of the solution as a whole, it being required that the total number of positive charges of whatever source (ions from water included) must equal the total number of negative charges. $[B^+]$ is the concentration of the cation of the salt, for example $[K^+]$ in a solution of potassium acetate. $[OH^-]$ can be eliminated from expressed inclusion in the equations by using the equation for the water equilibrium,

$$[H^+]\,[OH^-] = K_w \quad \text{or} \quad [OH^-] = \frac{K_w}{[H^+]}$$

These equations can be combined to yield (19) which, in logarithmic form, is (20)

$$K_a = \frac{[H^+]\left([B^+] + [H^+] - \dfrac{K_w}{[H^+]}\right)}{[S] - [B^+] - [H^+] + \dfrac{K_w}{[H^+]} - [s]} \qquad (19)$$

$$pK_a = pH + \log \frac{[S] - [B^+] - [H^+] + \dfrac{K_w}{[H^+]} - [s]}{[B^+] + [H^+] - \dfrac{K_w}{[H^+]}} \qquad (20)$$

Let equation (20) now be applied in a specific case in order that the relative importance of each term may be shown numerically. We shall use the data of Walpole (1914) for mixtures of acetic acid and sodium acetate. The compositions of the solutions and the measured values of pH which Walpole gives are found in table 1. Lest false interpretations of the treatment be made, it should be emphatically stated that the values called pH are not strictly those of $\log \dfrac{1}{[H^+]}$. Partly for this reason and partly for the reason described in Chapter XI the constants as calculated should not be expected to be exactly the same for all ratios

of acetate to acetic acid. In Chapter XXV corrections will be discussed. With this caution we may proceed as if the cited values truly represent hydrion *concentrations*.

Again we shall proceed with the assumption that the concentration of undissociated salt, $[s]$, in this instance [sodium acetate], is negligible. This at once simplifies the treatment, because it not only eliminates this specific term but it also makes it

TABLE 1

Calculation of pK_a from Walpole's data for mixtures of acetic acid and sodium acetate

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
NaAc MOLAR	HAc MOLAR	pH	$[H^+]$	$[B^+] + [H^+]$ X	$[S] - [B^+] - [H^+]$ Y	LOG $\frac{X}{Y}$	pK_a	pK_a BY APPROXIMATION
0.000	0.200	2.696	0.00201	0.00201	0.198	-1.994	4.690	∞
0.005	0.195	3.147	0.00071	0.00571	0.1943	-1.532	4.679	4.739
0.01	0.19	3.416	0.00038	0.01038	0.1896	-1.262	4.678	4.695
0.02	0.18	3.723	0.00019	0.02019	0.1798	-0.950	4.673	4.677
0.04	0.16	4.047	0.00009	0.04009	0.1599	-0.601	4.648	4.649
0.06	0.14	4.270	0.00005	0.06005	0.1399	-0.367	4.637	4.638
0.08	0.12	4.454	0.00004	0.08004	0.12	-0.176	4.630	4.630
0.10	0.10	4.626	0.00002	0.10002	0.10	0.000	4.626	4.626
0.12	0.08	4.802	0.000016	0.12	0.08	0.176	4.626	4.626
0.14	0.06	4.990	etc.	0.14	0.06	0.368	4.622	4.622
0.16	0.04	5.227		0.16	0.04	0.602	4.625	4.625
0.18	0.02	5.574		0.18	0.02	0.954	4.620	4.620
0.1925	0.0075	6.024		0.1925	0.0075	1.409	4.615	4.615
0.1975	0.0025	6.518		0.1975	0.0025	1.898	4.620	4.620

possible to consider $[B^+]$ equal to the concentration of total sodium acetate.[12] Therefore the values of $[B^+] + [H^+]$, found in column 5 of table 1, are readily calculated from the experimentally determined values of $[H^+]$, column 4, and the values for total sodium acetate, column 1.

The reader may readily calculate, by using the value 10^{-14} for K_w, that the values of $\frac{K_w}{[H^+]}$ are so small as to be negligible in

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[12] No undissociated base, NaOH, is supposed to remain.

the sum in equation (20). Equation (20) now reduces practically to (21)

$$pK_a = pH + \log \frac{[S] - [B^+] - [H^+]}{[B^+] + [H^+]} \qquad (21)$$

With this there are made the remaining calculations, which are summarized in table 1 and which lead to the values of pK_a found in column 8.

There are cases in which values for $\frac{K_w}{[H^+]}$ are significant while those for $[H^+]$ are insignificant (alkaline solutions). In rare cases both terms have to be considered. The latter occur when the measurements are near "neutrality."

It will be noted in table 1 that values for $[H^+]$ in the lower part of the table affect the magnitude of the sum $[B^+] + [H^+]$ so little that the effect is there negligible. We can readily imagine two cases in which this neglect would be serious. One case would be that of a stronger acid maintaining, during the course of its treatment with a base, values of $[H^+]$ large in relation to $[B^+]$. Another case would be a solution so extremely dilute that $[B^+]$ would approach the magnitude of $[H^+]$.

A USEFUL APPROXIMATION

If we confine attention to the cases like that illustrated in table 1 we may, for purposes of approximation, neglect $[H^+]$ as it occurs in the sum $[B^+] + [H^+]$. Then equation (21) is further simplified to equation (22).

$$pK_a = pH + \log \frac{[S] - [B^+]}{[B^+]} \qquad (22)$$

which may be rewritten

$$pH = pK_a + \log \frac{[B^+]}{[S] - [B^+]} \qquad (22a)$$

This is virtually

$$pH = pK_a + \log \frac{[salt]}{[residual\ acid]} \qquad (23)$$

This is frequently called the Henderson-Hasselbalch equation. Compare (23) with (12b) on page 16 and see column 9, table 1.

We might return to the complete equation (20) and discuss in the general language of algebra the effects to be expected if probable values for the concentration of possibly undissociated salt [s] were introduced. The danger of this is two-fold. We would be discussing quantities which are *experimentally* evaluated with such difficulty and uncertainty that we would find the mere algebraic discussion rather academic. In the second place we might be led to emphasize a method of treating salts which is less profitable than that which will be discussed in later chapters.

DISTINCTION BETWEEN α-CURVES AND TITRATION CURVES

Equation (12a) is

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}$$

The "approximate equation" developed in a preceding section is

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

It has been shown in the case of acetic acid that, for a given set of conditions, there is a fair degree of agreement in the application of these two equations. However, if α be considered zero before any alkali has been added to an acetic acid solution in the course of its titration, it is obvious that the dissociation of the acetic acid is being neglected. No correspondence between the α-curve and the actual titration curve should be expected near the beginning of the titration.

This lack of correspondence becomes more and more emphasized as the "strength" of the acid being titrated increases. The case of hydrochloric acid is the extreme. In this case it is advisable to regard the acid as practically completely dissociated in dilute solution, and to be gradually eliminated as acid during the course of the titration.

This matter could be gone over again in detail with the aid of the equations discussed in previous sections. However, the student will probably find it more profitable at this point to compare the α-curves of figure 2 and figure 11 (page 47) with the titration curves of figure 92 (page 531).

AN EXAMPLE OF DILUTION

There may now be considered another aspect of the acetic acid-sodium acetate mixtures. In table 2 are tabulated Walpole's data for various dilutions of a solution *equimolecular* with respect to both the sodium acetate and the acetic acid used in constructing the mixtures.

By the approximation formula (23) an observed value of pH should equal pK_a, since the ratio $\dfrac{[salt]}{[acid]}$ is fixed and is equal to 1. In the calculations of pK_a shown in the table there has been used the more nearly complete formula (21). Its use in place of

TABLE 2

The apparent change of pK_a with dilution of a solution equimolecular with respect to both acetic acid and sodium acetate

(Data from Walpole (1914))

TOTAL ACETATE	NaAc	HAc	pH	$[H^+]$ $\times 10^5$	$\dfrac{X}{[B^+] + [H^+]}$ $\times 10^5$	$\dfrac{Y}{[S] - \dfrac{[B^+] -}{[H^+]}}$ $\times 10^5$	LOG $\dfrac{X}{Y}$	pK_a
0.4	0.2	0.2	4.606	2.48	$20,000^+$	$20,000^-$	0.000^+	4.606
0.2	0.1	0.1	4.623	2.38	$10,000^+$	$10,000^-$	0.000^+	4.623
0.08	0.04	0.04	4.646	2.26	4002.0	3998.0	0.000^+	4.646
0.04	0.02	0.02	4.663	2.17	2002.0	1998.0	0.001	4.662
0.032	0.016	0.016	4.673	2.12	1602.0	1598.0	0.001	4.672
0.02	0.010	0.010	4.684	2.07	1002.1	997.9	0.001	4.683
0.01	0.005	0.005	4.706	1.97	502.0	498.0	0.003	4.703
0.004	0.002	0.002	4.737	1.83	201.8	198.2	0.008	4.729
0.002	0.001	0.001	4.758	1.75	101.75	98.25	0.015	4.743

the first approximation (equation (23)) is not significant in this instance, except for the higher dilutions. Even then its use produces little improvement in the constancy of the "constant" pK_a. In general it is well, when dealing with highly dilute solutions, and especially with acids of low pK_a values, to consider the more complete formula. However, there remains a strong suggestion that account should be taken of the undissociated salt. We shall see in Chapter XXV that this question is now being dealt with by unique methods and that, starting with the postulate of practically complete dissociation of salts, the effect we now have

in mind is accounted for by interionic forces.   This is sometimes
described as a force which produces an ionic clustering.   These
only remotely resemble true salt molecules.   Therefore, we had
best not try to get the complete answer to our problem from the
elaboration of an equation which was established in the first in-
stance on simplifying assumptions and in ignorance of the de-
tailed nature of specific solutions.
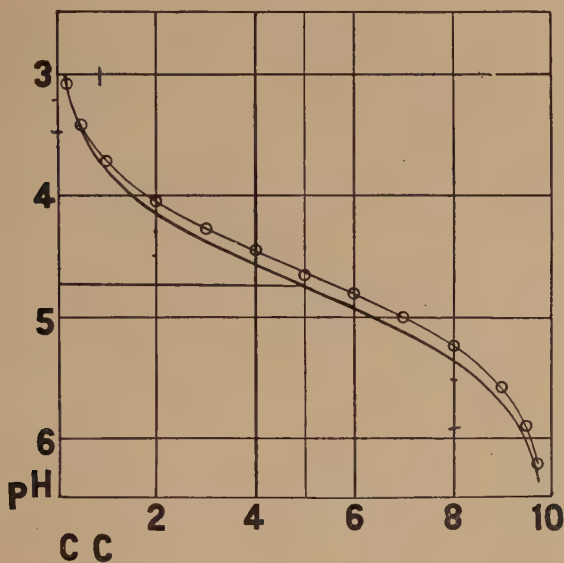
FIG. 3. TEN CUBIC CENTIMETERS 0.2 N ACETIC ACID TITRATED WITH
0.2 N NaOH

Experimental data shown by centers of circles (hydrogen electrode).
Type curve is shown centered at pH = 4.73 the ideal position as corrected
for solutions of zero ionic strength. See page 507.

Equation (23) may be considered a first approximation useful
for the treatment of weak acids.   Equation (21) may be con-
sidered a first approximation useful when [H$^+$] becomes of appre-
ciable magnitude relative to [S] and [B$^+$].

Figure 3 shows the experimental data for 0.2 N acetate mix-
tures and also, in a displaced position, the type curve drawn with
the aid of equation (21).   The placement of this type curve was
made with a value of pK$_a$ taken from conductivity data for

the dissociation constant of acetic acid.   As indicated in table 2, the value of pK_a, varies with the dilution.   We shall also see that it varies with the salt content and with the standard of reference chosen.   However, the general form of the curve and its approximate position are now our chief interests.

ACIDS WITH MORE THAN ONE REPLACEABLE HYDROGEN

Since it is not within the province of this book to outline all types of acid-base equilibria which are met in the application of methods for determining hydrion concentrations, the main principles have been illustrated by considerations of simple acids and bases.   The outline is easily extended to acids with more than one replaceable hydrogen and also to those compounds which contain both acidic and basic groups and which are called "amphoteric ionogens" or more usually "amphoteric electrolytes" or "ampholytes."   The extension will be illustrated graphically; but, to indicate the manner in which equations corresponding to the geometry are handled, one simple example will be given.

Assume an acid of type HAH dissociating stepwise to $\overline{HA}^-$ and $\overline{\overline{A}}$.
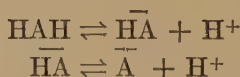
$$HAH \rightleftharpoons \overline{HA} + H^+$$
$$\overline{HA} \rightleftharpoons \overline{\overline{A}} + H^+$$

The equilibrium equations are:

First step
$$\frac{[\overline{HA}]\,[H^+]}{[HAH]} = K_1 \tag{24}$$

Second step
$$\frac{[\overline{\overline{A}}]\,[H^+]}{[\overline{HA}]} = K_2 \tag{25}$$

If secondary considerations discussed during the treatment of the simple systems are neglected, there is need to employ only one additional fundamental equation, namely that giving the sum [S] of the concentrations of all species.

$$[S] = [HAH] + [\overline{HA}] + [\overline{\overline{A}}] \tag{26}$$

By defining the degree of the first step of ionization by

$$\frac{[HA^-]}{[S]} = \alpha_1 \qquad (27)$$

and the degree of the second step by

$$\frac{[A^{--}]}{[S]} = \alpha_2 \qquad (28)$$

there are derived from the above the following:

$$\alpha_1 = \frac{K_1\,[H^+]}{K_1K_2 + K_1\,[H^+] + [H^+]^2} \qquad (29)$$

$$\alpha_2 = \frac{K_1K_2}{K_1K_2 + K_1\,[H^+] + [H^+]^2} \qquad (30)$$

The degree of total ionization, α_t, is evidently

$$\alpha_t = \frac{\alpha_1 + \alpha_2}{2}$$

Inspection of equations (29) and (30) shows that, since their denominators are the same, the relative values of $K_1[H^+]$ and of K_1K_2 determine whether, at a given value of $[H^+]$, α_1 or $1 + \alpha_2$ shall be the larger proportion of α_t.

The effects of varying the difference between K_1 and K_2 can be shown best indirectly by resorting again to logarithmic relations expressed *graphically*. However, actual *calculations* are performed most easily with the *equations* given above. In figures 4 to 6 are charted the curves for three, multivalent acids. Differences between the pK_a values are such as to show in figure 4 no serious deviations from the picture which three independent acids would give. In figures 5 and 6 are indicated "overlappings" to different degrees.

AMPHOLYTES

For amphoteric electrolytes (i.e., electrolytes containing acidic *and* basic groups) a relation of great importance may be illus-
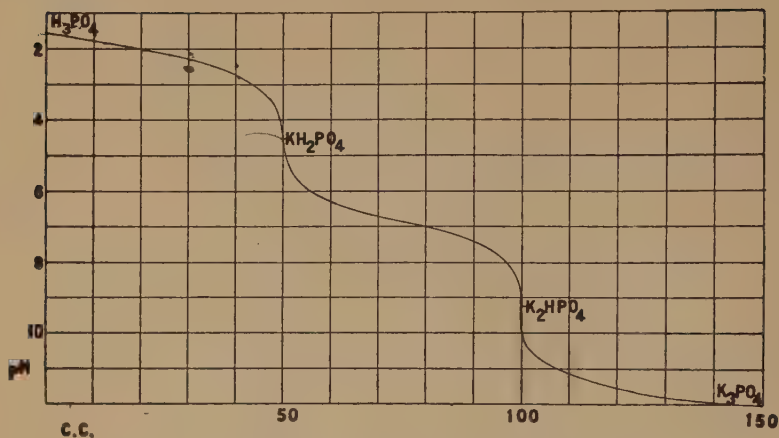
FIG. 4. TITRATION CURVE OF PHOSPHORIC ACID

Fifty cubic centimeters of $M/10$ H_3PO_4 titrated with $N/10$ KOH.   Shows step-wise "neutralization" of three hydrogens.
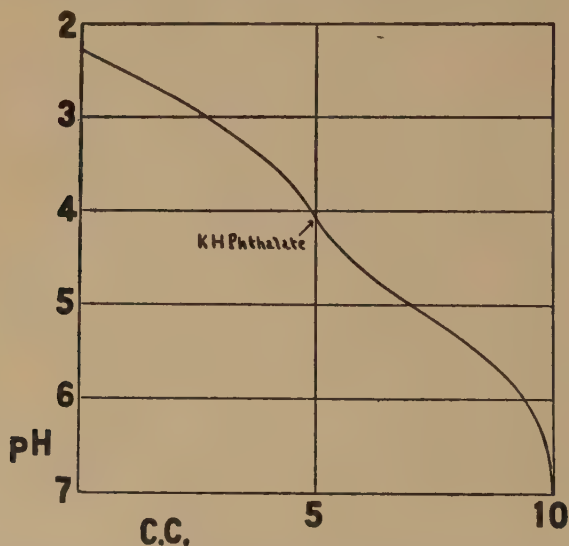
FIG. 5. TITRATION OF THE "DIBASIC" ACID, PHTHALIC ACID, WITH KOH
Shows step-wise neutralization but "overlapping" of titration curves

strated by the conduct of the simple ampholyte, p-amino benzoic acid. The acid dissociation constant K_a is 6.8×10^{-6} and the basic dissociation constant K_b is 2.3×10^{-12} (Scudder). Translating these into the corresponding pK values we have 5.17 and
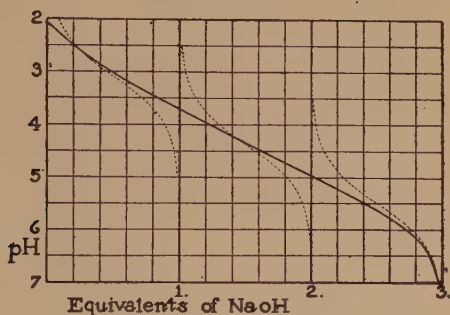
FIG. 6. TITRATION OF THE "TRIBASIC" ACID, CITRIC ACID

Shows that the pK_a values are sufficiently close to obscure the curvatures of the idealized curves for each step. (After Hastings and Van Slyke (1922).)

2.36.[13] If we regard the compound as if it were made up of an acid and a base with the above dissociation constants and each

p-amino benzoic acid   Cation   Anion

               in acid solutions   in alkaline solutions
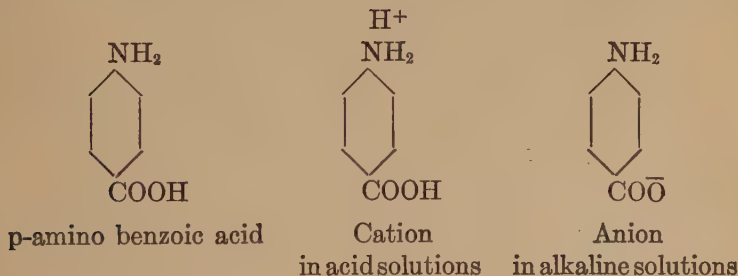
independent of the other, we can plot the dissociation curves of each with the aid of equations (12a) and (15a). In each case the dissociation-residue curves are the complements. These are plotted in figure 7 with heavy lines. It is seen that they cross at pH 3.77. This means that at pH 3.77 there is a maximum of undissociated residue. Now if the salts are more soluble

[13] See page 48.

than the free compound itself, there should be a minimum solubility at pH 3.77.   Michaelis and Davidsohn (1910) found a minimum solubility at pH 3.80.
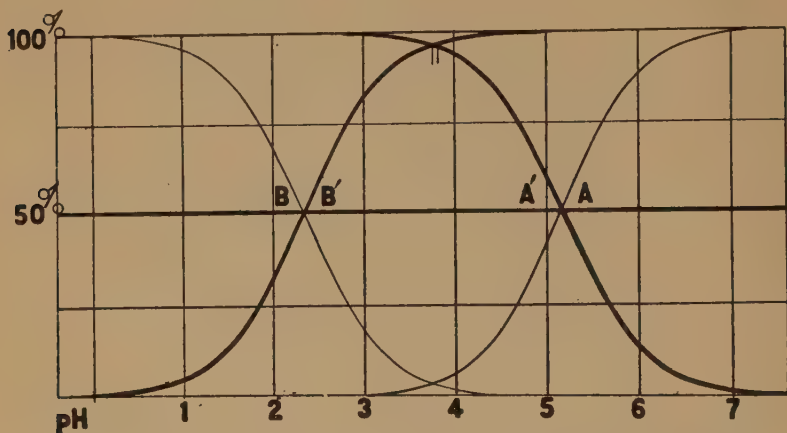
FIG. 7. DISSOCIATION CURVES, A AND B, AND DISSOCIATION-RESIDUE CURVES, A′ AND B′, FOR p-AMINO BENZOIC ACID

Treated as if this amphoteric ionogen were composed of an acid with pK$_a$ value of 5.17 and a base of pK$_b$ value defined by pK$_b$ = pK$_w$ − 2.36.

Turning to the light lines A and B of figure 7, we see that their intersection is at a point where the percentage of the compound ionized as an anion is equal to the percentage ionized as a cation. In other words the amount carrying a negative charge is equal to the amount carrying a positive charge.   Because of this equality the point where it occurs is called the *isoelectric point*.

If we still maintain the simple conditions postulated in this elementary treatment, we can calculate the isoelectric point from the dissociation constants of an amphoteric electrolyte.

Consider an amphoteric electrolyte of the type HROH for which we have the following equilibrium equations:

$$\frac{[HR^+]\,[OH^-]}{[HROH]} = K_b \tag{31}$$

$$\frac{[ROH^-]\,[H^+]}{[HROH]} = K_a \tag{32}$$

When $[HR^+] = [ROH^-]$ (isoelectric condition)

$$K_b \frac{[HROH]}{[OH^-]} = K_a \frac{[HROH]}{[H^+]} \tag{33}$$

Hence $\qquad\qquad [H^+] = \sqrt{\dfrac{K_a}{K_b} K_w} \qquad\qquad (34)$

In the case cited above $[H^+] = \sqrt{\dfrac{6.8 \times 10^{-6}}{2.3 \times 10^{-12}} 10^{-14}}$

or $pH = \log \dfrac{1}{[H^+]} = 3.77$

Furthermore from equations (31) and (32)

$$[HR^+] + [ROH^-] = K_b \frac{[HROH][H^+]}{K_w} + K_a \frac{[HROH]}{[H^+]}$$

If we let $[HR^+] + [ROH^-] = X$, X becomes a minimum when

$$\frac{d\,X}{d\,[H^+]} = 0, \text{ a condition fulfilled when } [H^+] = \sqrt{\frac{K_a}{K_b} K_w}$$

In other words the sum of the anion and cation concentrations is a minimum at the isoelectric point.

Only in case $K_a = K_b$ will the isoelectric point correspond with the "neutral point," pH 7.0.

It is at once evident that the isoelectric point of an amphoteric electrolyte is a point at or near which there should tend to occur maximal or minimal properties of its solution. Indeed at such points have been found to occur minimum solubilities, minimum viscosities, minimum swelling, optimum agglutinations, etc.

Lest this exposition obscure matters of importance to the treatment of complex ampholytes, the reader should consult such papers as that of Sørensen and Linderstrøm-Lang (1927).

See Levene and Simms (1923) on calculation of isoelectric points.

In figure 7 the treatment is as if for two distinct substances, one an acid and the other a base. Actually the acidic group and the

basic group are in the same molecule. When the simultaneous equations are solved for the identical dissociation residue and this is charted, its curve will follow B′ and A′ for the most part but will pass from B′ to A′ a little below the intersection of B′ and A′.

Figure 8 gives another set of cases.

It will be noted that this elementary outline of the subject of ampholytes has been presented with the aid of a specific case in which the ion formed is probably the univalent anion or the univalent cation according to the pH value of the solution. Many ampholytes probably ionize in such a way as to form "hybrid"[14] ions of the type $^+NH_3$–R–COO$^-$. These are called in the German *Zwitter-Ionen*, signifying hermaphroditic ions. They
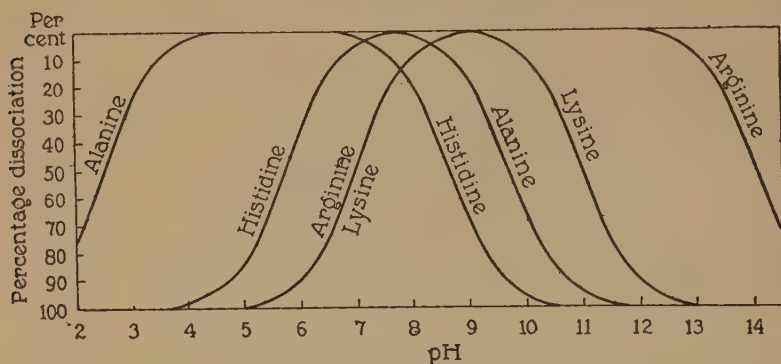
FIG. 8. REPRESENTATION OF THE DISSOCIATION CURVES OF HEXONE BASES
(After Foster and Schmidt (1923))

are often called ampholyte ions with the implication of the above special significance of opposite gender or of hybrid nature. Perlzweig (1926) uses the term "amphoteric ion."

As previously suggested, experimental methods do not always show clearly whether an acid or a base is being handled; and by the same token it is often uncertain whether an ionization constant assigned to an ampholyte from the measurements has been properly formulated as an acid constant or should be reformulated as a basic constant. Thus the reformulation of the so-called acid and basic constants of certain amino acids will depict these

[14] Kolthoff and Furman (1926, p. 49), use the term "hybrid ion."

compounds as existing as hybrid ions at the isoelectric point instead of as undissociated molecules. For a more detailed discussion of this matter see Bjerrum (1923).

It should be emphasized that the foregoing relationships have been developed from very simple conditions. When these conditions have been approached, experimental verification has been found. The insight thus gained has led to a better understanding of complex ampholytes, the complete equilibria of which can be seen only in broad outline.
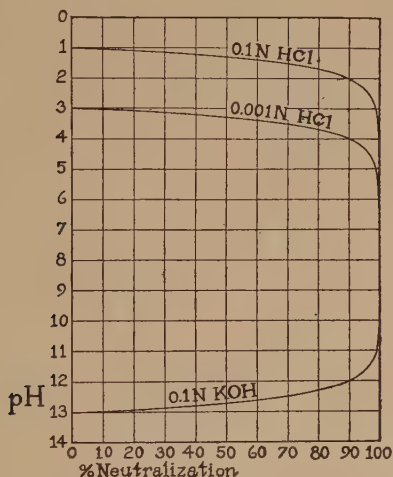
FIG. 9. TITRATION CURVES OF HYDROCHLORIC ACID AND POTASSIUM HYDROXIDE

"STRONG" ACIDS AND BASES AND THEIR SALTS

Many acids like hydrogen chloride (and bases like sodium hydroxide) are so near complete dissociation in dilute solution that a first approximation in their treatment can be accomplished by assuming complete dissociation. The hydrion concentration is then assumed equal to the concentration of the substance. If a solution of hydrogen chloride is under consideration and is progressively undergoing "neutralization" by potassium hydroxide, there is obtained actually a picture of the relation of pH to degree of "neutralization" similar to one or the other of the

curves in figure 9. These curves were calculated on the assumption that $[H^+] = [$"unneutralized" HCl$]$. A similar curve for the titration of KOH is also shown in figure 9.

However, if the solution vary in its initial content of one or another neutral salt, or vary, as it actually does during titration, in the proportion of neutral salt, a distinctly appreciable departure from the approximately calculated relations noted above will be found when the hydrogen electrode method of measurement is used. Fundamentally the effect is not very different from the "residual error" already noted when hydrogen electrode measurements are carried into the elementary treatment of a mixture of a weak acid and its salt. But in the present instance we are dealing with a strongly dissociating acid and in respect to the high degree of dissociation the acid is like salts such as KCl. The high concentration of the acid's charged ions produces an effect as truly as the highly dissociating salts produce their effects. Therefore, the displacement of the actual curve from that approximately calculated cannot be ascribed solely to a "*salt-effect.*" Rather should it be called an evidence of the conduct of strong electrolytes in general.

This is a subject which has stimulated many investigations and has led to still incomplete but very illuminating results. The modern treatment is unique but a discussion of it must be postponed. However, we need not be troubled for the time being. Although we have introduced simplifying assumptions restricting too free and generalized application of the equations, these serve admirably to outline the main features of the subject. To only a little less degree are we safe in outlining the conduct of solutions of strong acids and bases by the assumption of complete dissociation. Later we shall return to detail.

CHAPTER II

SOME SPECIAL ASPECTS OF ACID-BASE EQUILIBRIA

Words are the footsteps of reason.—FRANCIS BACON.

Many relations implicit in the general equations of acid-base
equilibria do not appear vivid and do not find their way into
everyday practice until they are reargued, reformulated and
named. A consequence is a special terminology which must be
understood if the literature is to be followed intelligently; for
sometimes a whole subdivision of our subject is summed up in
a single expression.

THE pH SCALE

As a normal solution of an acid has been defined as one con-
taining in 1 liter of solution the equivalent of 1.008 grams of
acidic hydrogen, so the normal solution of the hydrogen ion was
defined to be one containing in 1 liter of solution 1.008 grams
of hydrogen ions.

Thus an acid solution may be described in terms of its normal-
ity with respect to total acid or in terms of its normality with
respect to hydrions.

To distinguish between these two components with their com-
mon unit it has been suggested that we call "normality" in its
older sense the *quantity* factor of "acidity" and the hydrogen
ion concentration the *intensity* factor. This may serve to em-
phasize a distinction, but the suggested analogy with the quantity
and intensity factors of energy is confusing when we retain for
each a unit of the same category. Nevertheless the two com-
ponents remain in a restricted sense the quantity and intensity
factors of "acidity." The one is the total quantity of available
acid. The second, the concentration of the hydrogen ions, repre-
sents the real intensity of "acidity" whenever it is the hydrogen
ion which is the more directly active participant in a reaction.
This is admirably expressed when we use for hydrogen ion con-
centrations a mode of expression which links it with the *potential*

of a hydrogen electrode. It so happens that in determining the hydrogen ion concentration with the hydrogen electrode the potential of this electrode is put into an equation which reduces to the form:

$$\frac{\text{Potential}}{\text{numerical factor}} = \log \frac{1}{[H^+]}$$

Later we shall see that this potential, expressed in volts, is the intensity factor in the free-energy change involved in the transport of hydrions from a concentration of one normal to another given value of $[H^+]$. Thus the expression $\log \dfrac{1}{[H^+]}$ is a linear function of an *intensity* factor of energy-change and in this sense it can be called an index to acid intensity.

On the other hand the association of the words "potenz" and "puissance" with pH arose in a totally different manner. In his original article Sørensen (1909) says:

. . . . , la grandeur de la concentration des ions hydrogène s'exprime par le facteur de normalité de la solution par rapport aux ions hydrogène, facteur indiqué sous la forme d'une *puissance*[1] *négative* de 10.

Dans tous les cas traités dans le présent memoire . . . .

. . . . le facteur de normalité de la solution sous le rapport des ions hydrogène ou, en d'autres termes, le nombre d'atomes-grammes d'ions hydrogène par litre est plus petit que 1 et peut être posé égal à 10^{-p}, où pour le nombre p je propose *le nom d'exposant des ions hydrogène et la désignation* p_H. Par *exposant des ions hydrogène* (p_H^+) d'une solution, nous entendons donc *le logarithm Brigg de la valeur réciproque du facteur de normalité* de la solution *relativement aux ions hydrogène*.

Comme il n'est d'ordinaire pas question de solutions d'ions hydrogène plus fortes qu'une solution normale, j'ai choisi la définition ci-dessus de l'exposant des ions hydrogène, qui par suite sera généralement un nombre positif; il ne sera négatif que dans les cas bien rares où l'on a affaire à des solutions plus fortes que la normale.

Thus p_H^+ is defined by the relation:

$$p_H^+ \equiv \log_{10} \frac{1}{[H^+]}$$

As a matter of typographical convenience we shall use pH in place of the original p_H^+ and P_H^+.

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[1] "Potenz" in the German translation, i.e., power (mathematical).

If we follow Sørensen's original suggestion, pH may be called the hydrogen ion exponent. Its numerical magnitudes have been called "Sørensen values," "reaction numbers," etc. The term exponent (puissance, Potenz, power) is employed because the relation

$$pH = \log_{10} \frac{1}{[H^+]}$$

or

$$pH = -\log_{10}[H^+]$$

may be written $[H^+] = 10^{-pH}$. Here $-pH$ appears as an exponent.

TABLE 3

Relation of $[H^+]$ to pH

$[H^+]$	pH	$[H^+]$	pH
10^{+1}	-1	10^{-7}	7
$10^{\pm0}$	0	10^{-8}	8
10^{-1}	$+1$	10^{-9}	9
10^{-2}	2	10^{-10}	10
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-12}	12
10^{-5}	5	etc.	
10^{-6}	6		

A caution may now be noted. A difference of sign occurs between a given value of pH and the exponent found when the normality of the corresponding hydrogen ion concentration is written in the usual way. For example, -7 is the exponent in 10^{-7}; but the pH value corresponding to $[H^+] = 10^{-7}N$ is $+7$.

The gross relation of $[H^+]$ to pH is shown in table 3. See also table B, appendix (page 673).

The convenience of pH over $[H^+]$ is manifest when we compare the numerical values encountered in chemical and physiological studies. For instance, one enzyme may operate most actively at a hydrogen ion concentration of 0.01 normal while another is most active at 0.000,000,001 normal. While convenient abbreviations of such unwieldy values are 1×10^{-2} and 1×10^{-9}, there remains the difficulty of plotting such values on ordinary

cross-section paper. If the difference between 0.000,000,001 and 0.000,000,002 is given a length of one millimeter, the difference 0.01 to 0.02 when plotted on the same scale would be ten kilometers, ten kilometers distant. Evidently the logarithmic spacing should be followed and fortunately it is the logarithmic plotting of hydrogen ion concentration (in terms of pH) which correctly depicts the fact that the difference between 1×10^{-9} and 2×10^{-9} may be as important to one set of equilibria as the enormously greater difference between 1×10^{-2} and 2×10^{-2} is to another set of equilibria. This is revealed in the charts on previous and subsequent pages.

Thus both convenience and the nature of the physical facts invite us directly or indirectly to operate with some logarithmic function of [H+].

It is unfortunate that a mode of expression so well adapted to the treatment of various relations should conflict with a mental habit. [H+] represents the hydrogen ion concentration, the quantity usually thought of in conversation when we speak· of increases or decreases in acidity. pH varies inversely as [H+]. This is confusing.

The normality mode of expression has historical priority and consequently conventional force. Since there is a hydrogen ion concentration for each hydroxyl ion concentration it became the custom, following Friedenthal (1904), to express both acidities and alkalinities in terms of [H+]. This gave a scale of one denomination and the meaning of "higher" and of "lower" became firmly fixed. Later we meet the new scale with its direction reversed. The inconvenience is unquestionable and partly because of this the pH scale has been criticized.

Wherry[2] (1919, 1927) and others have proposed changes of one kind or another which they believe introduce greater simplicity or convenience. Wherry (1927) in particular has urged the use of his "active acidity" [antilog (7.0 − pH)] and the descriptive terms: *superacid* (pH 3 to 4), *mediacid* (pH 4 to 5), *subacid* (pH 5 to 6), *minimacid* (pH 6 to 7), *neutral* (pH 7), *minimalkaline* (pH 7 to 8), etc. His purpose is admirable and his case well stated. It is, in short, an attempt to "humanize" the statement of acidity for the benefit particularly of botanists.

It will presently be indicated that we are not denying the excellence of the *purpose* if we classify Wherry's proposal with others. We may pass over the fact that the functions offered are arbitrary and artificial. The same may be said of pH. We may pass over the fact that one or the other

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[2] Compare Wherry and Adams (1921) with reply by Clark (1921). See also Giribaldo (1925), Derrien and Fontès (1925), Guillaumin (1926), Richter (1926), Kolthoff (1926), Lambling.

of these newer functions, offered as a convenience, would entail the extreme inconvenience of recasting in a new mold a vast amount of accumulated data now recorded in terms of pH. The fundamental difficulties with all the new functions so far proposed are these. Some of them involve a new basis of reference when we are having difficulty enough with the conventional basis (see Chapter XXIII). It might be said that the choice, for instance, of "neutrality" as a reference point is made without involving those refinements which acquaint us with the shifts of the "neutral point" and is made for purposes of approximate descriptions only. As in all matters of definition the choice is permissible. However, its proposal is as much as to say that the proposer has no anticipation that his follower will see farther than he sees and will have no need to reëstablish contact with the refinements he has ignored. Those substitutes for pH, which have been proposed so far, employ so many unacknowledged complexities and tacit assumptions that they have not commanded assent.

If simplicity be desired, it were better to ignore the special meanings of pH, $[H^+]$, a_H, etc., which these various authors have used in deriving their new functions; it were better to ignore the almost useless "neutral point," and to develop the themes of Chapters XI and XXVII. It would probably not satisfy the novice merely to tell him that a pH value is to be used as an arbitrary *number* representing the *state* of acids in solution but if he will use indicators as type acids he can *visualize something* of what the numbers mean. He would then be relieved of the puzzling question of how a concentration of $\frac{1}{1,000,000}$ N can so profoundly affect the things he deals with and he might consent to use the numbers with the conventional name of pH. Because the subject is important too much effort cannot be spent upon making the presentation direct, simple and at the same time representative of actuality. This is certainly not accomplished by piling one convention upon another, one mathematical function upon another, one difficulty upon another. Until a really fundamental and simple change is proposed, attempts to alter what has become established convention should be vigorously opposed and the convenience of pH should be preserved.

In passing it may be noted that occasionally a mind is found which honestly distrusts the use of a logarithmic function of $[H^+]$ because it is logarithmic. Apparently it demands $[H^+]$ itself from a sense of absolutism. One possessed of this obsession might profitably consider the innumerable phenomena which are most vividly described by use of logarithmic functions. See, for example, the absorption of light by an indicator solution as described in Chapter VII. But see in particular Chapter XXVII.

A new symbol, pa_H, has been suggested by Sørensen and Linderstrøm-Lang (1924) to indicate a function of hydrion *activity* in contrast to pH which is a function of hydrion *concentration*. This will be discussed on page 479.

While discussing "pH" we may note that a symbolization originating in Sørensen's pH is coming into wide use. In Chapter I it is noted that,

when a dissociation constant occurs in an equation in the form $\log \frac{1}{K_a}$, it has become the custom to write $\log \frac{1}{K_a}$ as pK_a. So also the custom is spreading to similar functions and we find, for instance, pI^-, indicating the logarithm of the reciprocal of iodide ion concentration.

THE EFFECT OF DILUTION

The effect of dilution upon the hydrogen ion concentration of a solution may be briefly generalized by some approximations.

Consider an acid of the type HA for the dissociation of which we have the equilibrium equation:

$$\frac{[H^+] \times [A^-]}{[HA]} = K_a$$

If K_a is small there must obviously be a large reserve of undissociated acid so long as the concentration of total acid is high. As the solution is diluted this reserve dissociates to keep K_a constant; but there is a readjustment of all components which can be conveniently followed only by means of the simple algebraic equation expressing the equilibrium condition.

If the acid alone is present in the solution we may assume that $[A^-] = [H^+]$. Also if $[S_a] = $ the total acid, $[HA] = [S_a] - [H^+]$.

Substituting these in the above equation and solving for $[H^+]$ we have:

$$[H^+] = \sqrt{K_a[S_a] + \frac{K_a^2}{4}} - \frac{1}{2} K_a$$

When K_a is small in relation to $[S_a]$

$$[H^+] \cong \sqrt{K_a[S_a]}$$

Compare the equation on page 13. On these assumptions the hydrogen ion concentration should vary with dilution of the solution (diminution of S_a) only as the square root of $K_a[S_a]$.

If there is present a salt of the acid we can apply the equation derived on page 22 which shows that the hydrogen ion concentration of a mixture of a weak acid and its highly dissociated salt

is determined approximately by the ratio of acid to salt. Since dilution does not change the ratio, such a mixture should not suffer a change of hydrogen ion concentration beyond the limits set by the approximate treatment with which this relation was derived.

Therefore, except for solutions of high hydrogen ion concentration induced by the presence of unneutralized strong acids, the hydrogen ion concentration should vary with dilution somewhere between the zero change indicated by the last approximation and the square root relation first indicated.

If an acid be one which, in pure solution, is completely dissociated, the hydrion concentration is equal to the analytical or stoichiometrical normality of the acid. This will not be shown *precisely* by the hydrogen electrode method of measurement since this device measures energy changes which are not strictly proportional to concentration changes. This appears in a striking way when a solution of hydrochloric acid is concentrated. At some dilutions the hydrion concentration, as calculated with the aid of the uncorrected formula for the concentration cell, will appear to be higher than that of the available acid. This aspect will be discussed later.

In the case of mixtures of weak acids and their salts, dilution may in many instances produce changes in hydrion concentration too small to be detected by any but refined methods. Advantage of this is taken in the dilution of solutions otherwise too dense optically for the application of the indicator method.

The effect of dilution should be reconsidered after reading the last part of Chapter XXV.

TABLE 4

Effect of dilution

MOLECULAR CONCENTRATION OF GLYCOCOLL	pH	MOLECULAR CONCENTRATION OF ASPARAGINE	pH
1.0	6.089	1.0	2.954
0.1	6.096	0.1	2.973
0.01	6.155	0.01	3.110
0.001	6.413	0.001	3.521
0.0001	6.782	0.0001	4.166

For bases and amphoteric electrolytes relations similar to those discussed above may be deduced.

One or two actual cases may be of interest. Sørensen has given the accompanying table (table 4) of the pH values of different dilutions of asparagine and glycocoll.

The dilution here is ten-fold at each step, yet the increase in pH is very small while the solutions are between 1.0 and 0.01 M.

Walpole (1914) besides giving data on the hydrogen electrode potentials of various dilutions of acetic acid and "standard acetate," has determined the effect of a twenty-fold dilution of various acetic acid-sodium acetate mixtures. The change of pH on twenty-fold dilution of standard acetate is about 0.08 pH; and for mixtures of acetic acid and sodium acetate which lie on the flat part of the curve the change of pH is of the same order of magnitude. When the ratio $\frac{\text{acetic acid}}{\text{sodium acetate}}$ reaches 19/1 the change is about 0.3 pH.

See Cohn (1927) and page 509 on the dilution of phosphate solutions.

The brief outline given above takes no account of changes of equilibrium which sometimes occur in colloidal solutions.

"NEUTRALITY" AND VALUES OF K_w

It was shown in Chapter I that, *under ideal conditions*, the product of the hydrogen ion concentration and the hydroxyl ion concentration of an aqueous solution is constant

$$[H^+][OH^-] = K_w$$

Therefore, aqueous solutions, even those containing large excess of hydrogen ions (i.e. strongly acid solutions) must contain sufficient hydroxyl ions to maintain the constant relation shown above. Likewise aqueous solutions, even those containing large excess of hydroxyl ions (i.e. strongly alkaline solutions), must contain sufficient hydrogen ions to maintain the constant relation shown above. Obviously, there will be one point at which the concentration of hydrogen ions will equal the concentration of the hydroxyl ions, that is $[H^+] = [OH^-]$. Using for K_w the rounded value 10^{-14}, we find this point as follows.

$$[H^+]^2 = [OH^-]^2 = 10^{-14} \text{ or } [H^+] = [OH^-] = 10^{-7}$$

In other words, equality of hydrion and hydroxyl ion concentrations occurs at pH $= 7$. This is, as stated, an approximation. Here no account has been taken of the variation of the value of K_w with variation of temperature, salt-content of the solution, etc., nor of the precise meaning of the values called K_w as they are derived from experimental measurements of very different types.

Considerable confusion will be avoided if there is maintained a categorical as well as an obviously numerical distinction between K_w and the pH value called "neutrality."

The pH value 7.0 is a *convenient* reference point with which to differentiate "acid" from "alkaline" solutions in ordinary, crude descriptions. Otherwise, it is of little practical significance. To be sure, it is the pH value of pure water and, therefore, an interesting value to *calculate* as a *derivation* from water's characteristic constant, K_w. But pure water itself has seldom been seen and is of little use. Its hydrogen ion concentration has no general relation to the hydrogen ion concentration at the equivalence point sought in the "neutralization" of an aqueous solution of an acid by an aqueous solution of a base. This will be made plain in the discussion of the theory of titration (Chapter XXVIII) but it also appears in several of the figures of Chapter I. "Neutrality" is also of no interest whatever in the study of ampholytes. See Chapter I.

In contrast to the pH-value 7, K_w, the ionic product of water, is frequently employed when formulations of equilibria involve both hydroxyl and hydrogen ions. The relation $[H^+][OH^-] = K_w$ enables one to eliminate either $[OH^-]$ or $[H^+]$ when desired. Usually the necessity of this transformation may be avoided as will be shown in the discussion starting on page 46.

K_w has been determined by a variety of methods and with substantial agreement. The following are some instances.

Kohlrausch and Heydweiller (1894) determined the electrical conductivity of water approaching very near to purity. On the assumption that the conductance is proportional to the numbers and mobilities of the hydrogen and hydroxyl ions, that these are present in equal concentrations and that the mobilities of the hydrogen and hydroxyl ions are known, there can be calculated the value of K_w. Wijs (1893) used the results of a study of the

relative rates of hydrolysis of methyl acetate by hydrions and hydroxyl ions and applied these data to the case of the hydrolysis of methyl acetate by water. There have also been studies of the hydrolysis of salts, studies on the hydrogen potential in acid and alkaline solutions (e.g., Lewis, Brighton and Sebastian (1917)) and many other studies leading to substantially the same order of magnitude for K_w.

Kolthoff (1921) has compiled the following table 5 showing the "dissociation" constant of water at different temperatures as given by different authors. Lewis, Brighton and Sebastian (1917) found $K_w = 1.012 \times 10^{-14}$ at 25°C. Hence, $[H^+] = 1.006$

TABLE 5

Ion-product (dissociation constant) of water at different temperatures
(After Kolthoff and Furman (1926))

TEMPER- ATURE	AUTHORITIES			
	1	2	3	4
°C.				
0	0.12×10^{-14}	0.14×10^{-14}		0.089×10^{-14}
18	0.59×10^{-14}	0.72×10^{-14}	0.74×10^{-14}	0.46×10^{-14}
25	1.04×10^{-14}	1.22×10^{-14}	1.27×10^{-14}	0.82×10^{-14}
50	5.66×10^{-14}	8.7×10^{-14}		
100	58.20×10^{-14}	74.0×10^{-14}		48.0×10^{-14}

1. Kohlrausch and Heydweiller (recalculated by Heydweiller) (1909).
2. Lorenz and Böhi (1909).
3. Michaelis (1914), p. 8.
4. Various investigators.

$\times 10^{-7}$ (practically, pH = 7.0). Lewis and Randall (1923) give $K_w = 1.005 \times 10^{-14}$ at 25°C.

The following values of pK_w (log $\frac{1}{K_w}$) given by Michaelis (1922) (see table 6) were obtained on a basis somewhat different from that used by Lewis, Brighton and Sebastian.

Here it may be said that K_w appears as a constant because, in its derivation, there was introduced at the very beginning the postulate that the environment is to be constant. If the solution be altered, as by the addition of a certain quantity of neutral salt, there is the possibility that K_w will have a new value under

the new conditions. It is only on the expectation that the altera-
tion will be slight in ordinary changes of composition that we are
justified in neglecting the corrections which modern theoretical
methods have brought to light. However figure 10 will illustrate

<div align="center">

TABLE 6

Interpolated values of $-log\ K_w$

(After Michaelis (1922))

</div>

TEMPERATURE	LOG $\dfrac{1}{K_w}$	pH OF NEUTRAL POINT
°C.		
16	14.200	7.10
17	14.165	7.08
18	14.130	7.07
19	14.100	7.05
20	14.065	7.03
21	14.030	7.02
22	13.995	7.00
23	13.960	6.98
24	13.925	6.96
25	13.895	6.95
26	13.860	6.93
27	13.825	6.91
28	13.790	6.90
29	13.755	6.88
30	13.725	6.86
31	13.690	6.85
32	13.660	6.83
33	13.630	6.82
34	13.600	6.80
35	13.567	6.78
36	13.535	6.77
37	13.505	6.75
38	13.475	6.74
39	13.445	6.72
40	13.420	6.71

what is to be expected. Note the specific effects of salts so similar
as are sodium chloride and potassium chloride.

At this point it is appropriate to remark that, since in exact
treatments of equilibria a correction term for K_w (or varying
activity coefficient for water, see later chapters) must be taken
into consideration, it will be well to formulate the *elementary*

aspects of our subject by avoiding forms which include K_w wherever that is feasible. This will be our policy in dealing with bases, although the classical equations will also be shown. The variation of K_w constitutes one of very many reasons for avoiding several of the schemes which have been suggested as substitutes for the pH scale (see p. 39) and which involve K_w in their derivations.

Although a correction term must be applied in refined formulation and although this correction term varies with every change in the composition of the solution, the rounded values of K_w as given by Michaelis (1922) and shown in table 6 may be used for ordinary, approximate calculations.
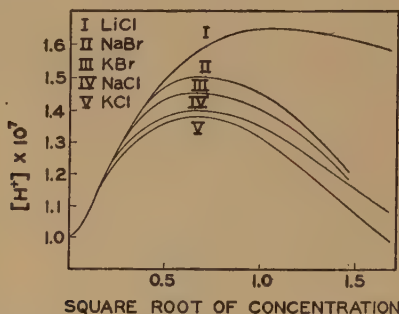
FIG. 10. VARIATION OF $\sqrt{K_w}$ WITH CONCENTRATION OF SALT

FORMULATION OF EQUILIBRIA IN SOLUTIONS OF BASES WITH AVOIDANCE OF THE USE OF [OH$^-$] AND K_w

In Chapter I figure 2 was constructed by first formulating the equilibria of acids and of bases separately and then aligning the two sets of curves by use of the relation

$$pH + pOH = pK_w = 14$$

In such a system of formulation the transformation of a given value of pOH to a corresponding value of pH (or *vice versa*) may be made whenever desired by use of that numerical value of pK_w which is applicable to the specific conditions. Therefore, it is convenient in general discussion to neglect pOH and to use pH uniformly.

Now consider figure 11 in conjunction with figure 2 (page 16). In figure 11 there is shown by curve C the relation between pH and percentage dissociation-residue for an acid having the dissociation curve B. Obviously curve C has the *form* of the dissociation curve for a base. Its position on the pH scale is made evident by the legend of figure 11.

Thus, if it suits our convenience, we may proceed to deal with the cation of a base as if we were dealing with the dissociation
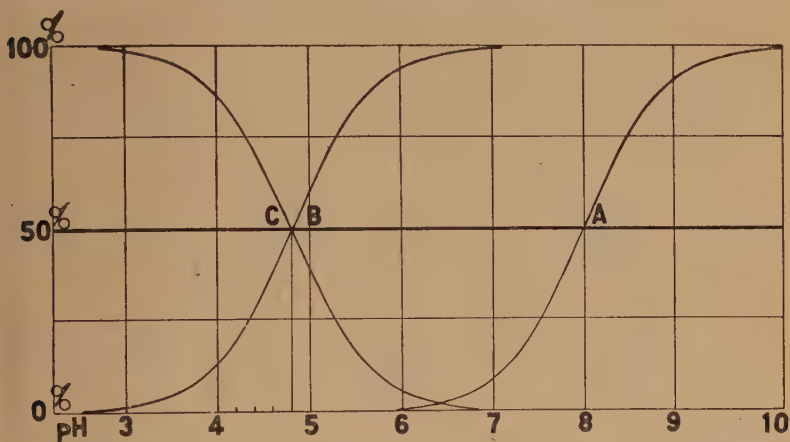
FIG. 11. DISSOCIATION CURVES AND DISSOCIATION RESIDUE CURVES
A. Dissociation curve for acid, $pK_a = 8.0$.
B. Dissociation curve for acid, $pK_a = 4.8$.
C. Dissociation curve for base, $pK_b = 14 - 4.8 = 9.2$ or dissociation-residue curve for acid $pK_a = 4.8$.

residue of an acid. Likewise we may deal with the dissociation residue of a base as if we were dealing with the anion of an acid. Likewise if our knowledge of a compound tells us nothing of its acidic or basic nature and if a series of measurements can be formulated by equation (12a) or by equation (15a) we shall not be able to tell by these measurements and their formulation whether we are dealing with an acid or a base.

However, there is a more direct way of arriving at a uniform method of formulation. Consider, for instance, equilibria in solutions of ammonia.

Ammonia, NH_3, is usually considered the parent of the base

NH_4OH, a hypothetical substance supposed to be formed by the hydration

$$NH_3 + H_2O \rightarrow NH_4OH$$

A basic dissociation constant could be defined by

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b$$

If this were used, we would proceed in the classical manner. Ammonia systems may equally well be treated in accordance with the following formulation[3]

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a$$

---

[3] It is instructive to note the following:

For the hydration equilibrium:

$$\frac{[NH_3][H_2O]}{[NH_4OH]} = K_h$$

For the dissociation equilibrium:

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b$$

Combine these two equations to yield:

$$\frac{[NH_3][H_2O]}{[NH_4^+][OH^-]} = \frac{K_h}{K_b}$$

Introduce $[H^+][OH^-] = K_w$

$$\frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_h K_w}{K_b [H_2O]}$$

If $[H_2O]$ is regarded as a constant

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a$$

There are many amino compounds which are substituted ammonias,—primary, secondary and tertiary ammonias. These may be considered to add hydrions and the equilibrium equation can be formulated as is done in the last equation above. We have also to consider the quaternary ion, $R_1R_2R_3R_4N^+$. In this case it would seem more logical to formulate the basic dissociation as follows

$$\frac{[R_1R_2R_3R_4N^+]\,[OH^-]}{[R_1R_2R_3R_4NOH]} = K_b$$

But the quarternary ammonium hydroxides are exceedingly strong bases. Frequently they are so strong that complete dissociation may be assumed as it is in the case of sodium and potassium hydroxides. Under such circumstances equations of the ordinary type are of little practical value as stated on page 12. The majority of the weak organic bases may be treated as the ammonia system is above and the equilibrium equation may be written

$$\frac{[R_1R_2R_3N]\,[H^+]}{[R_1R_2R_3N^+H]} = K_a$$

Thereby one avoids the necessity of considering either $[OH^-]$ or K_w.

The important point is that in general either mode of treatment can be adapted to *convenience*. When a more comprehensive formulation capable of extension to all sorts of non-aqueous solutions is desired, those presented by Brønsted (1923) and by Lewis in *Valence* will be found useful. See also Lowry (1924).

This is the equation given in the text where K_a is substituted for the constant

$$\frac{K_b\,K_w}{K_b\,[H_2O]}$$

This way of avoiding an account of the changing properties of the solvent is, in a sense, only a "dodge."

BUFFER ACTION

If we were to add to 1 liter of perfectly pure water of pH 7.0, 1 cc. of 0.01N HCl, the resulting solution would be about pH 5.0 and very toxic to many bacteria. If, on the other hand, we were to add this same amount of acid to a liter of a standard beef infusion medium of pH 7.0, the resulting change in pH would be hardly appreciable. This power of certain solutions to resist change in reaction was commented upon by Fernbach and Hubert (1900) who likened the resistance of phosphate solutions to a "tampon." The word was adopted by Sørensen (1909) and in the German rendition of his paper it became "Puffer" and thence the English "buffer." There has been some objection[4] to this word so applied, but it now possesses a clear technical meaning and is very widely used. By buffer action is meant the resistance to change of pH exhibited by a solution when it is subjected to gain or loss of acid or alkali. The elementary theory of buffer action is already clear if the implications of the simple equations of Chapter I are understood.

Returning to figures 4 to 6 we see that along the flat portion of a titration curve considerable alkali has to be added to produce much change in pH. Conversely, the addition of a strong acid would not have anywhere near the effect at this flat portion of the curve that it would have near either end. Thus it is evident that a mixture of an acid and its salt will tend to stabilize the pH of the solution only within certain narrow zones having vague boundaries. Mixtures buffering the solution within such a pH zone are often referred to as "regulator mixtures." They are of very great value to the analyst and the physiological chemist in that they furnish a means of stabilizing the hydrogen ion concentration within a predetermined zone. The middle point of this zone, where the strongest buffer action is exerted, is determined approximately as shown on page 17 by the dissociation constant of the acid or base concerned. Other things being equal, the choice of mixtures is thus revealed in a table of dissociation constants.

[4] "Moderator" is sometimes preferred. Moore, Roaf and Whitley were employing the concept as early as 1905 under the term "balanced-neutrality."

Henderson (1908) and Washburn (1908) simultaneously utilized
the principle that an equimolecular mixture of an acid and its
salt will stabilize the hydrion concentration of a solution.

Emphasis may be placed upon one or another aspect of buffer
action by means of the following examples.

A 1 per cent solution of Witte peptone was found to have a
pH value of 6.87.   To equal portions of the solution were added
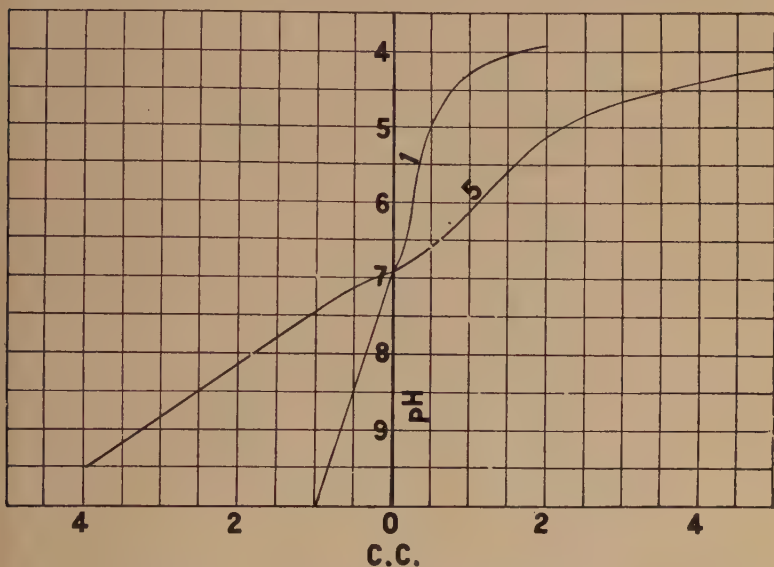
FIG. 12. TITRATION CURVES OF 1 PER CENT AND 5 PER CENT PEPTONE
SOLUTIONS

Ten cubic centimeters of peptone solution titrated with 0.1 N lactic
acid (to right) and with 0.1 N NaOH (to left).

successively increasing amounts of 0.1N lactic acid and the result-
ing pH was measured in each case.   There were also added to
equal portions of the solution successively increasing amounts of
0.1N NaOH and the resulting pH was measured in each case.
The pH values were then plotted on cross section paper as ordi-
nates against the amount of acid or alkali added in each case as
abscissas.   This gave curve 1 shown in figure 12.   The other
curve shown in this figure was constructed with data obtained
with a 5 per cent solution of Witte peptone.

Figure 12 shows that the buffer action of a solution is dependent upon the concentration of the constituents. The 5 per cent solution is much more resistant to change in pH than the 1 per cent solution.

It will also be noticed that in either case the buffer action is not the same at all points in the curve. In other words the buffer action can not be expressed by a constant but must be determined for each region of pH. This is illustrated even more clearly by the titration curve for phosphoric acid (fig. 4, page 28). At the point where the solution contains only the primary phosphate
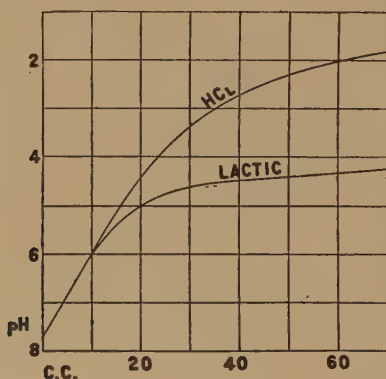
FIG. 13. TITRATION OF A BEEF-INFUSION CULTURE MEDIUM
· One hundred cubic centimeters of medium titrated with 0.2 N HCl solution in one case and with 0.2 N lactic acid solution in the other case.

and again where it contains only the secondary phosphate there is very little buffer effect indeed.

Furthermore the buffer action of a solution may not be due entirely to the nature of the initial constituents titrated but also to the nature of the substance with which it is titrated. This point may be illustrated by titrating a beef infusion medium in the one case with hydrochloric acid and in the other case with lactic acid, both of the same normality (see fig. 13). It will be seen that at first the two curves are identical. As the region is approached where the dissociation of the lactic acid (a weak acid) is itself suppressed because of the accumulation of lactate ions (and the hydrogen ions) further addition of this acid has com-

paratively little effect. The "strong" acid, hydrochloric, on the other hand continues to be effective in changing pH until at high hydrion concentrations the logarithmic function suffers less change. As already noted in Chapter I, hydrochloric acid may be considered in approximate treatments as completely dissociated. The flattening of the titration curve, of which pH is the ordinate, is therefore inherent in the nature of the case; but it must not be presumed that a mere mathematical limitation obscures the reality of a physically significant buffer effect. Imagine an acid which is not totally dissociated but which has a high dissociation constant. The degree of its dissociation remains a function of pH and if we are to suppress its dissociation completely we might have to run the pH value of the solution into negative values by adding high concentrations of very strong acids. Ultimately we reach a limit in the "strength" of the acids available and can use only higher total concentrations of those acids which approach complete dissociation in dilute solution.[5]

These examples will suffice to make it evident that the buffer action of a solution is dependent upon the nature and the concentration of the constituents, upon the pH region where the buffer action is measured and upon the nature of the acid or alkali added.

The main aspect of the subject is summed up in the relation $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$. This implies that, so long as the ratio $\frac{[A^-]}{[HA]}$ does not depart far from unity, $[H^+]$ cannot depart far from the constant K_a.

Buffer action, that is resistance to change of pH upon addition or loss of acid or alkali, cannot always be so easily formulated. For instance, suppose that there is present in a solid phase some material which adsorbs from the solution a component of the solution's acid-base equilibrium. That substance, by reason of its ability to take up or give off the adsorbed component according to the concentration of the component in the liquid phase, may act as a buffer. Henderson (1909) called attention to this. Bovie (1915) and others have shown the buffering effect of charcoal.

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[5] Later we shall encounter the case of an acid dye which behaves as if it has a dissociation exponent, pK = 1.5. To obtain what appeared to be complete dissociation there was used 36 per cent HCl solution!

When a component of the acid-base equilibrium of a solution reaches such a concentration that it precipitates and forms a solid phase in equilibrium with the liquid phase, the zone of pH, within which buffer action would be expected from the relations for homogeneous solutions, may be considerably altered. The direction which the treatment then takes is outlined on page 582

Since the types of such cases are numerous, we shall not pause to discuss the detail; but it should be noted that the subject is of fundamental importance to many problems of physiology, analysis, etc.

There are occasions when a more elegant definition of buffer action leads to very useful formulas. Thus Van Slyke (1922),
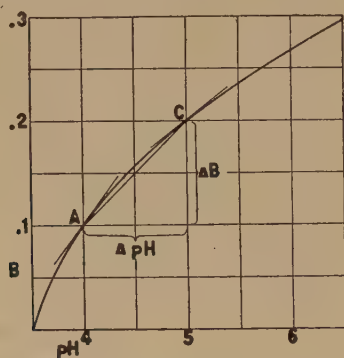
Fig. 14. Buffer Action
Change of pH on addition of base

in an independent development of a treatment first attempted by Koppel and Spiro (1914) (cf. Lehmann, 1922, and Michaelis and Perlzweig, p. 106) proposes the following.

Let there be charted as in figure 14 the relation between pH and the equivalents of base per liter added to a given solution. Between the points A and C the ratio $\dfrac{\Delta B}{\Delta(\text{pH})}$ gives the slope of the line AC. This is only a rough indication of the order of magnitude of the slope of a tangent to the curve in this region. The slope of the tangent obviously changes between its position at A and its position at C. To obtain the slope at any point use is made of the infinitesimals dB and d(pH).

Van Slyke then describes a unit for the buffer effect. "The unit adopted is the differential ratio $\frac{dB}{d(pH)}$, expressing the relationship between the increment (in gram equivalents per liter) of strong base B added to a buffer solution and the resultant increment in pH. Increment of strong acid is equivalent to a negative increment of base, or $-dB$. In these terms *a solution has a buffer value of 1 when a liter will take up 1 gram equivalent of strong acid or alkali per unit change in pH*. If base is added to a solution, pH is increased, so that both dB and $d(pH)$ are positive. If acid is added both dB and $d(pH)$ are negative. The ratio $\frac{dB}{d(pH)}$ is, therefore, always a positive numerical value."

To summarize Van Slyke's treatment we shall proceed as follows:

For the convenience of the mathematical treatment equation (12a) of Chapter I, namely,

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}$$

is rewritten with natural logarithm as (1)

$$pH = pK_a + 0.4343 \, ln \frac{\alpha}{1 - \alpha} \tag{1}$$

The derivative is

$$d(pH) = 0.4343 \, \frac{1 - \alpha}{\alpha} \, d\left(\frac{\alpha}{1 - \alpha}\right) \tag{2}$$

Whence

$$\frac{d\alpha}{d(pH)} = 2.303 \, \alpha(1 - \alpha) \tag{3}$$

When $\alpha = 0.5$, $\frac{d\alpha}{d(pH)} = 0.576$. This value is the maximum obtained by a univalent acid.

Now under limited conditions, explained in Chapter I,

$$\alpha = \frac{\text{Base added}}{\text{Total acid}} = \frac{[B]}{[S]} \text{ and } d\alpha = \frac{d[B]}{[S]}$$

Hence

$$\frac{d[B]}{d(\text{pH})} = 2.303 \, \alpha(1 - \alpha) \, [S] \qquad (4)$$

Also

$$\alpha = \frac{K_a}{K_a + [H^+]}$$

Hence

$$\frac{d[B]}{d(\text{pH})} = 2.303 \, [S] \frac{K_a[H^+]}{(K_a + [H^+])^2} \qquad (5)$$

For brevity $\frac{d[B]}{d(\text{pH})}$ is called β by Van Slyke. In figure 15 equation (5) is used to obtain part of the curve showing the relation of β to pH in the cases of 0.1 M and 0.2 M acetic acid. Equation (5) gives that part of each curve shown in the figure by the central, peaked portion and continued as dotted curves near pH 2 to 3.5. In the region lower than pH 3.5 correction must be made for the buffer effect of the strong acid. Likewise beyond pH 10 the effect of a strong base should be considered.

These additional buffer effects are calculated as follows.

Consider a strong base added to water. Assume that the base is completely dissociated. Then $d[B] = d[OH^-]$ and

$$\frac{d[B]}{d(\text{pH})} = \frac{d[OH^-]}{d \log [OH^-]} = 2.303 \, [OH^-] \qquad (6)$$

Likewise for the case of a strong acid added to water we have:

$$\frac{d[B]}{d(\text{pH})} = 2.303 \, [H^+] \qquad (7)$$

The buffer effect in strong acid or alkaline solutions is the sum of these two effects; i.e.,

$$\frac{d[B]}{d(pH)} = 2.303 \, ([H^+] + [OH^-]) \tag{8}$$

This is illustrated in figure 15.

Between pH 2 and pH 3.5 a resultant of the β of the acetate system and the β of the strong acid prevents the buffer index from falling to zero.
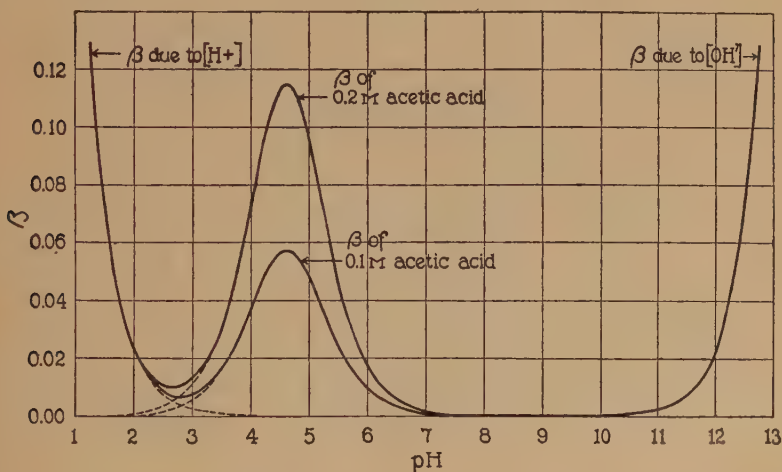
FIG. 15. VALUES OF $\dfrac{dB}{dpH}$ OR β FOR MIXTURES OF ACETIC ACID AND ACETATE
(After Van Slyke (1922))

For further details see the original articles by Van Slyke (1922), Koppel and Spiro (1914) and Täufel and Wagner (1926).

One very distinct advantage in the use of Van Slyke's buffer values arises from the fact that the buffer values of various component systems of a complex system are additive. When the individual values of component systems can be precisely formulated, much can be predicted of complex systems.

A FURTHER REMARK ON STRONG ELECTROLYTES

The reader who is seeking an outline of our subject will doubtless be willing to proceed with the approximate treatment which

was accorded strong acids at the close of Chapter I (page 34) and to postpone a reconsideration of the effects of those highly dissociating salts formed by the addition of strong bases to weak acids. Since it has been intimated that the simple relations presented so far are inapplicable to strong acids and bases, an additional remark on strong electrolytes may be appropriate here, pending the development in later chapters of more suitable methods of approach and formulation.

In the introductory section of Chapter I brief mention was made of the electronic architecture of atoms and molecules. There it was stated that certain compounds behave *as if* one of
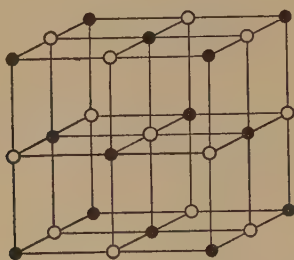
FIG. 16. REPRESENTATION OF A PORTION OF A CRYSTAL OF SODIUM CHLORIDE

Sodium ion represented by dots; chloride ion by circles

the component atoms has completely captured the valence electron or electrons of the other component with the result that the compound is virtually an *association of ions*. For example, it is believed that, whatever may be the orbits of the electrons in sodium chloride, the chlorine there found has captured an electron to complete its own octet, while the sodium has lost an electron. Consequently the sodium chloride molecule might be represented by $(Na^+, Cl^-)_x$. Indeed x-ray analysis of the crystal suggests this. An *interpretation* of the x-ray "reflection spectrum" of sodium chloride crystals yields the conclusion that the sodium and the chloride ions are arranged as shown in figure 16. In this picture there is no indication of the molecule NaCl or of any "molecule" short of the crystal as a whole. There is only evidence of a spatial arrangement which can reasonably be accounted

for by the *assumption* that chloride and sodium ions are each attracting the ions of opposite charge with no exclusive, one-to-one pairing. A variety of data supports this view.

When the components of the crystal are dispersed, as in water solution, it would certainly be expected that the only discrete particles persisting as individuals would be the sodium and the chloride ions (undoubtedly combined with water molecules). Indeed evidence has been molding opinion to this view until it is rather widely although not universally accepted. Thus many treatises start with the assumption of the "complete dissociation of strong electrolytes."

This view by no means excludes the persistence of the attractive force which is so strongly manifest in the crystal. The operation of this force, theoretically, can not become completely negligible until the thermal agitation becomes exceedingly great (infinite temperature) or the dispersion by the solvent becomes exceedingly great (infinite dilution). In short, it must be supposed that at any given concentration of the sodium chloride solution, and notwithstanding the thermal agitation, there occur situations in which a sodium ion is surrounded by more chloride ions than by sodium ions or a chloride ion is surrounded by more sodium ions than chloride ions. This is to be regarded as an expression of the orienting force.

Thus there should exist, statistically, groupings very different in nature from the sodium chloride molecule specified in the classical equation:

$$\frac{[Na^+]\,[Cl^-]}{[NaCl]} = K$$

If one is convinced of this, he might say that an attempt to apply the above equilibrium equation proceeds in ignorance of the nature of sodium chloride and is no test whatever of the mass law.

With this *interpretation* of the data on crystal structure and with the support of various other types of evidence it is convenient to regard salts such as sodium chloride, and also acids such as HCl, as completely ionized in solution and to take account of the constantly changing associations of the ions by methods quite different from those which are employed in treating the cases where true molecules are probably formed.

We owe to Milner and particularly to Debye and Hückel the way in which statistical mechanics may be applied to this situation. The theory is outlined in Chapter XXV. However, it should be well understood that Debye and Hückel attempt to take account only of the effect of the *electrical* forces between the oppositely charged ions and that their theory has nothing to say about several other factors which may interfere with the application of the postulates entering the derivation of the simple, ideal, equilibrium equation. Since these factors are many and varied, it may be said that the student has the choice of attempting the impracticably rigid all at once or of setting up an ideal as a guiding principle in some such way as that which we have here attempted.

There is, however, another way of approaching the subject. We shall see that some of the methods to be described, notably that of the hydrogen electrode, are methods which measure energy changes. It is sometimes assumed that there is some definite relation between two concentrations of hydrions and the energy necessary to bring a mole of hydrions from one of the given concentrations to the other. In this assumption trouble begins. It could be avoided if we were content not only to leave the results of the measurement in terms of energy changes but also to formulate equilibrium conditions in these same terms and to eschew the employment of equations cast in terms of concentration. Since current thought is not yet wholly receptive to the extreme of this method of formulation we have the rather interesting situation that the so-called rigid formulations of the day are fundamentally those of the energy changes, but there is introduced a term, called *the activity*, which has been rather inaccurately described as a sort of corrected concentration.

In place of the equation

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a$$

where [ ] represents concentration, there is used the equation

$$\frac{(H^+)\,(A^-)}{(HA)} = K_a$$

where ( ) represents "activity."

Then the equations reduce to the *forms* we have been using

but with "activity" replacing "concentration." Formulation by "activity" is a *defined* application of rigid thermodynamics but the value of the activity of a substance varies with every change of condition and practically makes concrete knowledge of the details largely empirical. Formulation by concentration is an idealistic application of molecular theory but then the equilibrium "constant" varies with every change of condition and again the detail remains largely a matter of empiricism.

We shall proceed with "concentrations" and molecular theory and shall return in due time to a consideration of energy changes.

THE SIGNIFICANCE OF CERTAIN pH VALUES

There is no hesitation in attributing a significance of actuality to hydrion concentrations arising from the dissociation of strong acids. There is little disposition to question the essential reality of hydrion concentrations arising from the dissociation of moderately weak acids. However, there is good reason to doubt the physical significance of hydrion concentrations said to be of the magnitude of 10^{-7}N, 10^{-13}N, etc.

We shall postpone a discussion of this very pertinent question to a later chapter because there will then be an opportunity to include material discussed in the intervening chapters. We may here state that if the questioned values be considered as numbers, they serve admirably and conveniently as *indices* to states of equilibrium among relatively large quantities of materials. If the doubting reader is not content to accept this for the moment as a dogma, he should at once read the first part of Chapter XXVII.

CHAPTER III

Outline of a Colorimetric Method

In a short time you will improve, my friend,
When of scholastic forms you learn the use;
And how by method all things to reduce.
Mephistopheles to the Student in Goethe's Faust.

While the word "indicator" can have various meanings,—as current indicator, pressure indicator, etc.,—we shall use it as a generic name for substances which "change color" when the pH values of their solutions change.

We shall postpone to a later chapter a closer analysis of what is meant by "change of color" and shall use the expression as it is commonly understood.

Each indicator exhibits color-change within a characteristic zone of pH. We shall consider here only those indicators which have one, or at most two, characteristic zones. Beyond one indefinite edge of such a zone one characteristic color appears. Beyond the other indefinite edge the other characteristic color appears. Within the zone, the color may be treated as if it were a mixture of the two characteristic colors. Because the edges of the zone are indefinite the color or color mixture in the center of the pH-zone constitutes a useful point of reference. The value of pH at the 50 per cent transformation is called the indicator's pK value. This originates in the use of the equation

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}$$

and in the treatment of the indicator as a simple acid.

The color chart is useful as a crude representation of the colors of various indicators at various values of pH. The pK values are indicated.

The color chart exhibits only intermediate colors. When the pH value of a solution containing any one indicator is lower than the pK value by about 2 units pH, what is conveniently called

the "acid color" appears. When the pH value of the solution is greater than the pK value of the indicator by about 2 units pH, what is conveniently called the "alkaline color" appears. "Acid" and "alkaline" used in this sense have no reference to a line of demarkation between "acid" and "alkaline" solutions. Theory associates the "acid color" with the "acid-form" and the "alkaline-color" with the "alkaline-form" of the indicator substance. These terms are conveniences.

In ordinary titrations (see Chapter XXVIII) conditions are so chosen that when the "end-point" of the titration is reached the pH value of the solution plunges through the entire range of the indicator's color transformation. A pronounced change of color occurs on the addition of a very small amount of acid or alkali. The intermediate colors even if observed are not emphasized. However, the intermediate colors are important to our present purpose.

They can be maintained by buffer solutions which maintain constant values of pH. Thereby reference standards may be prepared. Standard buffer solutions are described in Chapter IX. In their use it is essential to remember that the buffer solution controls only the *ratio*[1] between the concentrations of "acid" and the "alkaline" color-forms of the indicator. Therefore the preparation of a standard color tube to be judged by eye includes the use of a definite concentration of indicator substance and observation through a definite depth of solution.

Suppose that the phosphate-buffers are employed in the range pH 6.0 to pH 7.0 with the indicator brom thymol blue. If these standards are to be used in comparison with an unknown solution it is essential, not that any particular amount[2] of indicator be used, but that the *same* concentration be used in both standard and unknown. It is furthermore essential that standard and unknown be observed through *equal depths* of solution. It is then

---

[1] If instead of the ratio for the two color forms we use the ratio of the concentration of the alkaline color-form to the concentration of total indicator we may call this α and use the equation

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}.$$

[2] The amount becomes very important in studying poorly buffered solutions. See page 190.

clear that, if standard and unknown have produced the same ratio of the two color-forms of the indicator, the appearance of the two tubes will match. The first approximation of the theory concerned is that equal ratios of the two indicator forms will be produced by solutions of the same pH value. Therefore, if the color of the unknown match that of standard "pH 6.6" it is presumed that the pH value of the unknown is 6.6.

In case the approximate value of the unknown is undetermined a preliminary test may be made as follows. The indicator brom thymol blue will differentiate solutions having pH values greater or less than 7.0. If then, a drop or two of brom thymol blue gives a *distinctly* yellow color one knows that the solution has a pH value less than about 5.6. Imagine that brom cresol green is next tried and that there is found an intermediate color suggesting to the memory pH 4.4 or 4.6. Standards for this range are set up with phthalate buffers (table 35) or citrate buffers (table 39) and brom cresol green. The standards are compared with the unknown. It is remembered that equality of concentrations and views through equal depths are essentials. Suppose color match is not perfect at "4.4" or at "4.6" but that the unknown appears as if it would match an intermediate between standard "4.4" and "4.6." Unless extreme accuracy is desired 4.5 may be said to be the value for the solution under measurement.

In case an extensive set of standards is set up it is well to employ volumes, etc., systematically. Thus, 10 cc. of each buffer are added *seriatim* to each of a set of uniform test tubes and to each of these are added 5 drops of a stock solution of the proper indicator. Mixing should, of course, be insured. Now when an unknown is to be compared, 10 cc. of this solution are placed in a tube of the same bore as those of the standards and 5 drops of the stock indicator solution are added and mixed. Change of stock solution is obviously inadvisable.

When one is familiar with the colors of the indicators at known pH values, very fair estimations may be made without the aid of the standards; but there is no way as satisfactory as the setting up of the standards for the establishment of a correct impression of the relations of the various indicators on the pH scale. On the other hand, the author has discovered in his

T. B.
(ac)

1.2 1.4 1.6 1.8 ↑? 2.0 2.2 2.4 2.6 2.8

B. P. B
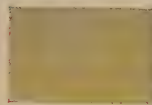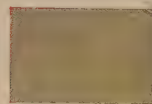
3.1 3.3 3.5 3.7 3.9 ↑ 4.1 4.3 4.5 4.7

B. C. G.
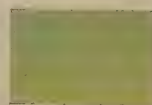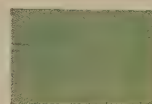
3.8 4.0 4.2 4.4 4.6 ↑ 4.8 5.0 5.2 5.4

C. P. R.
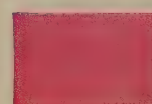
5.1 5.3 5.5 5.7 5.9 ↑ 6.1 6.3 6.5 6.7

B. C. P.
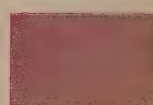
5.4 5.6 5.8 6.0 6.2 ↑ 6.4 6.6 6.8 7.0

Fig. 17. Chart Showing the Colors of Sulfonphthalein Indicators in Solutions of Known pH

B. T. B.	6.1	6.3	6.5	6.7	6.9	7.1	7.3	7.5	7.7
P. R.	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.4	8.6
C. R.	7.4	7.6	7.8	8.0	8.2	8.4	8.6	8.8	9.0
M. C. P.	7.4	7.6	7.8	8.0	8.2	8.4	8.6	8.8	9.0
T. B.	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6

conversations that there are many investigators who would like to use indicators for the occasional rough measurement of pH but who are discouraged by a pressure of work which prevents them from taking the time to carefully prepare the standard solutions. To furnish such investigators with a demonstration of the general relations of the various indicators and to furnish *rough* standards the attempt has been made to reproduce the colors in figure 17.

It must be remembered, however, that in undertaking a repro- duction by means of the printer's art the publishers are to be commended for their courage and are not to be held responsible for the inadequacy of the result. Aside from the inherent dif- ficulty in freeing a printed color from the effect of the vehicle, there remains the utter impossibility of reproducing with paper and ink the effect observed in a liquid solution. The funda- mental phenomena are *quantitatively* very different in the two cases. Therefore, the user of the chart of colors will have to use discretion and some imagination. If he does not attempt to make the reproductions take the place of the standards he should find them useful for class room demonstrations, for refresh- ing the memory and for *rough* standards.

For class-room work it is advantageous to show the position of the several indicators on the pH scale by cutting the chart and relining each series so that corresponding pH values overlap.

Many users of the color chart have not only failed to note the warning given above in previous editions of this book but have failed to realize how the best use may be made of the chart. By certain mechanical improvements in the art of production the *gradation* of the color has been improved. This feature serves as a very helpful guide. Too much emphasis should not be placed upon the color *quality*. These brief reminders give re- lease to the exercise of judgment which is all that the chart can aid.

In each case the colors were designed to match standards in tubes 16 mm, internal diameter containing 10 cc. of buffer solu- tions and the following proportions of indicators.

Thymol blue (T.B. ac)   1.0 cc. 0.04 per cent solution
Brom phenol blue (B.P.B.) 0.5 cc. 0.04 per cent solution
Brom cresol green (B.C.G.) 0.5 cc. 0.04 per cent solution

Chlor phenol red (C.P.R.)   0.5 cc. 0.04 per cent solution
Brom cresol purple (B.C.P.) 0.5 cc. 0.04 per cent solution
Brom thymol blue (B.T.B.) 0.5 cc. 0.04 per cent solution
Phenol red (P.R.)   0.5 cc. 0.02 per cent solution
Cresol red (C.R.)   0.5 cc. 0.02 per cent solution
Meta cresol purple (M.C.P.) 0.5 cc. 0.04 per cent solution
Thymol blue (T.B.)   0.5 cc. 0.04 per cent solution

CHAPTER IV

CHOICE OF INDICATORS

We are now forced to increase the number of compounds, not merely in order to prepare new substances, but to discover natural laws.—
R. FITTIG.

From the enormous number of colored compounds found in nature and among the products of the laboratory many have been called into use as acidimetric-alkalimetric indicators. Few have been chosen. Among indicators of plant origin litmus and alizarine are the more familiar. One indicator of animal origin, cochineal, an extract of an insect, was formerly used to some extent. Walpole's (1913) treatment of litmus, Walbum's (1913) study of the coloring matter of the red cabbage and some of the more recent work, have given us some data on properties of plant and animal pigments which are applicable to hydrogen ion determinations. But for the most part indicators of natural origin have been neglected for the study of "synthetic" compounds.

Litmus has played so important a rôle in acidimetry that it is worthy of brief, special mention.

Litmus is obtained by the oxidation in the presence of ammonia of the orcin contained in lichens, generally of the species *Roccella* and *Lecanora*. The material which comes upon the market is frequently in the form of cubes composed of gypsum or similar material and comparatively little of the coloring matter. The coloring matter is a complex from which there have been isolated many compounds, chief among which are azolitmin, erythrolitmin, erythroleïn and spaniolitmin. Of these the azolitmin is the most important. Scheitz (1910) found the azolitmin of commerce to be of uncertain composition and it may well be so now, for the composition of the crude material varies with the source and with the extent of the complex action of air and alkali on the original materials.

The following method of preparing a sensitive litmus solution is taken from Morse (1905).

67

The crushed commercial litmus is repeatedly extracted with fresh quantities of 85 per cent alcohol for the purpose of removing a violet coloring matter which is colored by acids but not made blue by alkalies. The residue, consisting mainly of calcium carbonate, carbonates of the alkalies and the material to be isolated, is washed with more hot alcohol upon a filter and then digested for several hours with cold distilled water. The filtered aqueous extract has a pure blue color and contains an excess of alkali, a part of which is in the form of carbonate and a part in combination with litmus. To remove the alkaline reaction the solution is heated to the boiling point and cautiously treated with very dilute sulfuric acid until it becomes very distinctly and permanently red. Boil till all CO_2 is dispelled. Treat with a dilute solution of barium hydroxide until the color changes to a violet. Filter, evaporate to a small volume and precipitate the litmus with strong alcohol. Wash with alcohol and dry.

Dr. P. Rupp (private communication) prefers to make a final washing with water which removes much of the salt at the expense of some dye.

"Synthetic" indicators have for the most part displaced those of natural origin until litmus and alizarin, turmeric and cochineal are becoming more and more unfamiliar in the chemical laboratory. Indeed Bjerrum (1914) states that the two synthetic indicators, methyl red and phenolphthalein, particularly because of the zones of hydrogen ion concentration within which they change color, are sufficient for most titrimetric purposes.

But the two indicators mentioned above cover but a very limited range of hydrogen ion concentration so that they are insufficient for the purpose we now have under consideration. A survey of indicators suitable for hydrogen ion determinations was opened in Nernst's laboratory in 1904 by Salessky. This survey was extended in the same year by Friedenthal, by Fels and by Salm and the results were summarized in Salm's famous table (cf. *Z. physik. Chem.*, **57**, 471).

Then came the classic work of Sørensen (1909) of the Carlsberg laboratory in Copenhagen. The array of available indicators had become so large as to be burdensome. Sørensen in an extensive investigation of the correspondence between colorimetric and electrometric determinations of hydrogen ion concentrations revealed discrepancies which were attributed mainly to the influence of protein and salts. He chose those indicators which were relatively free from the so-called protein and salt errors, constructed solutions of known and reproducible hydrogen ion con-

centrations and thus furnished the biochemist with selected tools
of beautiful simplicity. It is well to emphasize the labor of
elimination which Sørensen performed because without it we
might still be consulting such tables as that published by Thiel
(1911), or the ponderous table 8, pages 76–86, and be bewildered
by the very extensive array.

Sørensen's work, coupled as it was with a most important con-
tribution to enzyme chemistry, gave great impetus to the use of
indicators in biochemistry. His selection was, therefore, soon
enlarged by additions of new indicators which fulfilled the criteria
of reliability which he had laid down. Alpha naphthol phthalein,
a compound first synthesized by Grabowski (1871), was shown by
Sørensen and Palitzsch (1910) to have a range of pH 7–9 and was
found useful in biological fluids. Methyl red (Rupp and Loose,
1908) was given its very useful place by the investigations of
Palitzsch (1911). Henderson and Forbes (1910) introduced 2–5
dinitrohydroquinone as an indicator possessing several steps of
color change and therefore useful over a wide range of pH.
Walpole (1914) called attention to several indicators of potential
value. Hottinger (1914) recommended "lacmosol," a constituent
of lacmoid, and Bogert and Scatchard (1916) advocated the use
of dinitrobenzoylene urea.

Lund (1927) and Kolthoff (1927) report some data obtained
with certain very interesting indicators of the triphenyl methane
series. These indicators are colored in acid solution and color-
less in alkaline solution. They are numbers 99a, 99b and 102a
of table 8. No. 102a is described as requiring a time interval for
the color change. The others are described as useful for a variety
of purposes. Their unique color changes should be of service
in some cases.

Additions continue to be made every little while; sometimes
with accompanying data of value to our subject. Only the cases
for which pH measurements of some kind are available can be
included in the following tables. For this reason the tables do
not include those vast arrays of material waiting to be explored.

In 1915 Levy, Rowntree and Marriott, without applying the
tests of reliability which Sørensen had employed, used phenol
sulphonphthalein in determining the pH of the dialyzate of
blood. This compound, first synthesized in Remsen's laboratory

by Sohon (1898), received considerable attention from Acree and his co-workers because it furnished excellent material for the quinone-phenolate theory of indicators. To further such studies Acree and White had synthesized new derivatives of phenol sulphonphthalein at the time when the work of Levy, Rowntree and Marriott attracted the attention of Clark and Lubs. The latter were looking for more brilliant indicators for use in bacterial culture media and were attracted by the well known brilliance of phenol sulphonphthalein. Through the courtesy of Professor Acree some of the derivatives which White had prepared were obtained. Many new homologs were synthesized by Lubs. There was then undertaken an extensive study of the applicability of these and numerous other indicators to the study of biological fluids and of bacterial culture media in particular. See Clark and Lubs (1916–1917). They finally selected a series of indicators which, for the most part, was made up of sulfonphthaleins. Two azo compounds were included, methyl red (cf. Palitzsch, 1911) and propyl red (Clark and Lubs, 1915). Propyl red precipitates too easily from buffer solutions and was soon discarded. Methyl red continued in the series until the work of Cohen (1922) [see especially Cohen's paper of 1927] made available several new sulfonphthaleins.

In the course of their investigations Clark and Lubs resurrected ortho cresol phthalein (Baeyer and Fraude, 1880), found it quite as reliable as phenolphthalein and more brilliant with a color better adapted to titrations in artificial light.

In spite of the fact that Sørensen rejected the greater number of the indicators which he studied and that Clark and Lubs, after a resurvey of the subject and the preparation of many new compounds, listed but few indicators as reliable, there has recently appeared a tendency to resurrect the rejects. Many of these are useful in special cases and undoubtedly there is an occasional individual to be found in the lists which has been insufficiently studied and unjustly rejected. Nevertheless, the indiscriminate use of miscellaneous indicators may lead to gross errors or at least to such a diversity of data that their correlation will become complex during the coming period when the specific salt-effects and general conduct of the individual indicators are still being determined.

It is, therefore, advisable to use the more thoroughly studied indicators. Three lists of these are given (tables 10, 11, and 12). The indicators therein listed should suffice for all ordinary needs. Sørensen's list is given in table 10 and to this are appended Sørensen's comments. For general purposes the indicators named in table 11 will be found the most satisfactory especially because of their brilliancy. Each of these, however, has its own special limitations as every indicator has. For the study of colorless solutions where salt errors are to be reduced the nitrophenols listed in table 12 should be valuable.

In table 8 are a few indicators which are undoubtedly reliable but little used, a few which are definitely unreliable though often used, and very many of uncertain character and for the most part bearing the stamp of disapproval by competent judges. Since the indicators in tables 10, 11 and 12 cover all ordinary requirements it seems hardly worth while to venture upon an analysis of table 8 except to note by a star one or another compound which seems promising or has received more or less careful study.

TYPE STRUCTURES

Since it is impractical to give structural formulas for all the indicators of the general list (table 8), a few typical structures will be given as guides. The grouping in table 7 is that of table 8 and the numbers are the index numbers of table 8.

COMMENTS ON THE GENERAL LIST

Table 8 is taken from International Critical Tables, Clark (1926). A few additions have been made. The lists on which it is based were originally compiled with the aid of Dr. Barnett Cohen and Dr. Elias Elvove with several purposes in view. In the first place there exist in the older literature a great many observations recorded in terms of the color of a given indicator. These data can often be translated into modern terms if the pH range of the given indicator is known. In the second place there are circumstances when, for one reason or another, it becomes necessary to draw upon the list of miscellany. It should therefore be available. Lastly, and perhaps most important, our review of the literature and of indicator labeling has shown that there is great confusion; and an initial step in the clarification of the subject

TABLE 7

Type structures shown by examples

EXAMPLES	GENERAL STRUCTURE
Nitro group	
12. p-Nitro phenol	HO—⬡—NO_2
16. Nitramine; 2,4,6-trinitrophenyl- methyl-nitroamine	O_2N—⬡—N with NO_2, CH_3, NO_2, NO_2
Mono-azo group	
44. Methyl orange; p-benzenesulfonic acid- azo-dimethylaniline	HO_3S—⬡—$N{=}N$—⬡—$N(CH_3)_2$
59. Methyl red; o-carboxybenzene-azo- dimethylaniline	⬡—$N{=}N$—⬡—$N(CH_3)_2$ CO_2H
Dis-azo-group	
87. Congo red; Diphenyl-disazo-bis-α- naphthylamine-4-sul- fonic acid	⬡—$N{=}N$— (naphthyl) NH_2, SO_3H ⬡—$N{=}N$— (naphthyl) NH_2, SO_3H
Triphenylmethane group	
97. Methyl violet 6B (penta- methyl constituent)	$(CH_3)_2$N—⬡ , CH_3 NH—⬡ , C, ⬡, $N{+}$ $(CH_3)_2$

TABLE 7—*Continued*

EXAMPLES	GENERAL STRUCTURE

Phthalein group

120. Phenol phthalein; dihydroxyphthalophenone

Sulfonphthalein group

142. Phenol red

Quinoline group

151. Quinoline blue; 1,1'-di-iso-amyl-4,4'-quinocyanine iodide

Indophenol group

152. Indophenol; Benzenone-indo-phenol

Azine group

158. Neutral red; Amino-dimethylamino-toluphenazonium chloride

Oxazine group

160. Alizarine green B; Dihydroxy-dinaphthaz-oxonium sulfonate

<p align="center">TABLE 7—Concluded</p>

EXAMPLES	GENERAL STRUCTURES
Anthraquinone group	
166. Alizarin; 1,2-dihydroxy-anthra-quinone;	
Indigo group	
168. Indigo carmine; Indigotin-5,5′ disulfonic acid	

will be taken if there is available a tabulation of existing data to serve as a basis for revision.

In examining a large collection of indicators the labeling was found to be insufficient in a large percentage of cases. On study-ing the literature we find evidence that others have encountered the same difficulty without stating so, for in many instances the indicator names given were evidently provided by one or another dealer who cared so little for the scientific uses of his commodity that he left from the label the designation essential to its identifica-tion. This habit had become more or less prevalent. In some instances our own uncertainty may be due to an arbitrary ad-herence to the nomenclature found in various editions of Schultz. For instance when we see the indicator croceïne listed and refer to Schultz (1914) we find four croceïnes with various distinguish-ing marks and seven other compounds for the names of which "croceïne" is used in one or another combination. But Schultz lists no *croceïne*. We are not helped in going back to the lists of Schultz and Julius (1902). Now we might assume that

"croceïne" was used in Salm's table as a term having a definite meaning outside the dye industry. On this principle we should find that "helianthine" has been employed in accordance with scientific usage. However we find that an old sample of helianthine from Salm's dealer is not the helianthine of methyl orange but corresponds in pH-range to Salm's Helianthine I, which, together with Salm's Helianthine II we have not identified.

There are other difficulties such as are illustrated by the case of Tropaeolin OOO No. 1 and Tropaeolin OOO No. 2. No. 1 is prepared from p-sulfanilic acid and *α-naphthol*. No. 2 is prepared from p-sulfanilic acid and *β-naphthol*. In this there is agreement by Schultz and Julius 1902, Green 1904 and Beilstein (third edition). In accord with this, Sørensen describes his α-naphthol preparation as Tropaeolin OOO No. 1. In the second edition of *Indicators and Test Papers*, Cohn (1914) has given synonyms for the α and β compounds which agree with Green, but has reversed the No. 1 and No. 2 at the headings of his descriptions and uses "No. 1" and "No. 2" inconsistently in the text. Prideaux (1917) has called the β compound Tropaeolin OOO and gives the range as 7.6–8.9, which looks suspiciously like Sørensen's 7.6–8.9 for the α compound. Prideaux uses the synonym Orange II for the β compound in harmony with Green; but on the next page describes the α compound as Orange II. The identity of Salm's Tropaeolin OOO is not clear. It was evidently different from the Tropaeolin OOO No. 1 used by Sørensen. We find that an old sample with the label "Tropaeolin OOO" agrees with neither Sørensen's nor Salm's data.

Many other instances might be cited to show the confused state of the subject. Because it is serious the reader will have to use the following tables with caution, and he need not be surprised if a sample of indicator which he tests does not give a pH range corresponding to that recorded. Since the publication of the list in the second edition only one person has called our attention to a correction. In this case the information was oral and unverified and hence is not applied. Established corrections will be welcome.

TABLE 8

General list of indicators

After Clark (1926)

The following list of indicators includes all those for which data on the pH-ranges have been found. Many of the data of this table are to be regarded with caution, because in some cases the names proposed are inadequate for complete indentification, and in other cases names have been given to materials of uncertain composition.

The Schultz (S....) and Rowe (R....) numbers are taken from the 1923 and 1924 editions, respectively, of these works. Delicate shades of meaning in the color nomenclature have been avoided, as data regarding the purity of the compounds have often been lacking. The abbreviations used are as follows: b, blue; br, brown; c, colorless; f, fades; fl, fluorescent; g, green; o, orange; p, pink; pu, purple; r, red; v, violet; y, yellow. pK is the pH at which there is an apparent half-transformation of the indicator. * indicates that the indicator has been studied in sufficient detail to be used in supplementing the lists of tables 10, 11 and 12.

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Nitro compounds		
1	2,4,6-trinitrophenol; Picric acid [S. 5; R. 7]....................	c 0.0– 1.3 y	(15, 21)
2	2,6-dinitrophenol [Michaelis' β]..	c 2.0– 4.0 y	(15, 20, 21)
3	2,4-dinitro-α-naphthol; Manchester yellow [S. 6; R. 9]......	y 2.0– 4.0 y	(3a)
4	2,4-dinitrophenol [Michaelis' α]...	c 2.6– 4.4 y	(17, 20, 21)
4a	4,6-dinitroguaiacol..............	pK = 3.4	(10, 17)
5	Dinitrohydroquinol.............	3–10	(11, 26)
6	Nitrohydroquinol...............	3–11	(26)
6a	3,5-dinitrocatechol.............	pK$_1$ = 3.25 pK$_2$ = 10.39	(17)
7	2,3-dinitrophenol [Michaelis' ϵ]...	c 3.9– 5.9 y	(15, 20, 21)
8	2,5-dinitrophenol [Michaelis' γ]...	c 4.0– 5.8 y	(15, 20, 21)
8a	2,4-dinitroresorcinol.............	pK = 4.22	(17)
9	2,6-dinitro-4-aminophenol; Isopicramic acid..................	p 4.1– 5.6 y	(36)
10	3,4-dinitrophenol [Michaelis' δ]...	c 4.3– 6.3 y	(20, 21)
11	4-nitro-6-aminoguaiacol..........	y 4.5– 8.0 r	(18)
12	p-nitrophenol....................	c 5.6– 7.6 y	(15, 20, 21, 32)
13	o-nitrophenol...................	c 5.0– 7.0 y	(26)
13a	2-nitroresorcinol................	pK$_2$ = 6.47	(17)
14	*Dinitrobenzoylene urea.........	c 6.0– 8.0 y	(2, 10)
15	m-nitrophenol...................	c 6.8– 8.6 y	(15, 20, 21)
16	2,4,6-trinitrophenyl-methyl-nitroamine; Nitramine.........	c 10.8–13.0 br	(15)
17	sym.-trinitrobenzene............	c 12.0–14.0 o; f	(10, 29)
18	2,4,6-trinitrotoluene............	p 11.5–14.0 o	(3a)

TABLE 8—*Continued*

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Mono-azo compounds		
19	p-toluene-azo-phenyl-aniline.....	1.0– 2.0	(31, 32)
20	p-carboxybenzene-azo-dimethyl-aniline; Para methyl red........	r 1.0– 3.0 y	(3, 33)
21	p-toluene-azo-phenyl-α-naph-thylamine......................	1.1– 1.9	(31, 32)
22	Benzene-azo-diphenylamine......	p 1.2– 2.1 y	(32)
23	m-benzenesulfonic acid-azo-diphenylamine; Metanil yellow [S. 134; R. 138]................	r 1.2– 2.3 y	(32)
24	Benzene-azo-phenyl-α-naphthyl-amine......................	v 1.4– 2.6 o	(31, 32)
25	p-benzenesulfonic acid-azo-di-phenylamine; Tropaeolin OO [S. 139; R. 143]...............	r 1.4– 2.6 y	(32, 33)
26	o-tuluene-azo-o-toluidine; Spirit yellow R [S. 68; R. 17]........	1.4– 2.9	(31, 32)
27	p-toluene-azo-benzyl-α-naphthyl-amine......................	1.6– 2.6	(31, 32)
28	p-toluene-azo-benzyl-aniline......	1.6– 2.8	(31, 32)
29	Benzene-azo-benzyl-α-naphthyl-amine......................	1.9– 2.9	(31, 32)
30	Benzene-azo-aniline; amino-azo-benzene [S. 31; R. 15]..........	y 1.9– 3.3 y	(31, 32, 33)
31	p-benzenesulfonic acid-azo-aniline...........................	r 1.9– 3.3 y	(31, 32, 33)
32	p-benzenesulfonic acid-azo-ben-zylaniline....................	r 1.9– 3.3 y	(32, 33)
33	m-carboxybenzene-azo-dimethyl-aniline......................	r 2.0– 4.0 y	(3b)
34	Benzene-azo-benzylaniline........	p 2.3–.3.3 y	(32)
35	p-benzenesulfonic acid-azo-m-chlorodiethylaniline............	r 2.6– 4.0 y	(32, 33)
36	m-nitrobenzene-azo-β-naphthol-3,6-disulfonic acid; Orange III [S. 47; R. 39].................	r 2.6– 4.6 y	(3a)
37	Benzene-azo-dimethylaniline; Töpfer's indicator [S. 32; R. 19].	r 2.9– 4.0 y	(32, 33)
38	o-carboxybenzene-azo-α-naph-thylamine.....................	r 2.9– 5.8 y	(34)
39	p-benzenesulfonic acid-azo-o-toluidine.....................	mid-point 2.9	(33)

TABLE 8—*Continued*

INDEX NUM-BER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Mono-azo compounds—*Continued*		
40	p-benzenesulfonic acid-azo-m-xylidine	mid-point 2.9	(33)
41	o-carboxybenzene-azo-diphenyl-amine	p 3.0– 4.6 y	(3b)
42	p-benzenesulfonic acid-azo-methylaniline	r 3.1– 4.2 y	(31, 32, 33)
43	p-benzenesulfonic acid-azo-ethyl aniline	r 3.1– 4.4 y	(31, 32, 33)
44	p-benzenesulfonic acid-azo-di-methylaniline; Methyl orange [S. 138; R. 142]	r 3.1– 4.4 y	(32, 33)
45	p-benzenesulfonic acid-azo-di-ethylaniline; Ethyl orange	r 3.5– 4.5 y	(31, 32, 33)
46	o-benzenesulfonic acid-azo-dimethylaniline	mid-point 3.5	(33)
47	p-benzenesulfonic acid-azo-m-toluidine	mid-point 3.5	(33)
48	p-benzenesulfonic acid-azo-p-xylidine	mid-point 3.6	(33)
49	* p-sulfo-o-methoxybenzene-azo-dimethyl-α-naphthylamine	b 3.5– 4.9 o	(23)
50	p-benzenesulfonic acid-azo-α-naphthylamine	r 3.5– 5.7 y	(32, 34)
51	p-benzenesulfonic acid-azo-phenyl-α-naphthylamine	v 3.5– 6.5 o	(34)
52	o-carboxybenzene-azo-phenyl-α-naphthylamine	v 3.5– 6.5 o	(34)
53	Benzene-azo-α-naphthylamine	r 3.7– 5.0 y	(32, 34)
54	p-toluene-azo-α-naphthylamine	3.7– 5.0	(31, 32)
55	o-carboxybenzene-azo-methyl-aniline	r 4.0– 6.0 y	(3b)
56	Benzene-azo-m-phenylenedi-amine; Chrysoidine [S. 33; R. 20]	o 4.0– 7.0 y	(3a)
57	o-carboxybenzene-azo-ethylani-line	r 4.2– 6.2 y	(3b)
58	o-carboxybenzene-azo-n-propyl-aniline	r 4.2– 6.2 y	(3b)
59	o-carboxybenzene-azo-dimethyl-aniline; Methyl red [R. 211]	r 4.2– 6.3 y	(4, 32, 33)
60	o-carboxybenzene-azo-diethyl-aniline; Ethyl red	r 4.4– 6.2 y	(3b, 33)

TABLE 8—*Continued*

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Mono-azo compounds—*Continued*		
61	* o-carboxybenzene-azo-di-n-propylaniline; Propyl red.......	r 4.6– 6.6 y	(3b)
62	o-carboxybenzene-azo-m-phenylenediamine..............	o 4.6– 7.6 y	(3a)
63	Benzene-azo-dimethyl-α-naphthylamine.....................	4.8– 5.5	(31, 32)
64	p-benzenesulfonic acid-azo-dimethyl-α-naphthylamine........	r 5.0–5.7 o	(31, 32, 34)
65	o-carboxybenzene-azo-α-naphthlyamine.................	p 5.6– 7.0 y	(3b)
66	o-carboxybenzene-azo-(di or mono?)-amyl aniline...........	o 5.6– 7.6 y	. (3b)
67	o-carboxybenzene-azo-dimethyl-α-naphthylamine..............	r 5.6– 7.6 o	(4, 34)
68	4-sulfo-α-naphthalene-azo-α-naphthol; Naphthylamine brown [S. 160; R. 175]...................	o 6.0– 8.4 p	(3a)
69	Tropaeolin?......................	y 7.0– 9.0 r	(29)
70	6-sulfo-α-naphthol-1-azo-m-hydroxybenzoic acid............	o 7.0– 8.0 b v 12 –13 r	(36)
71	Curcumine?......................	y 7.4– 8.6 b	(15)
72	p-benzenesulfonic acid-azo-α-naphthol; Tropaeolin OOO No. 1 [S. 144; R. 150]................	y 7.6– 8.9 p	(32)
73	p-benzenesulfonic acid-azo-β-naphthol; Tropaeolin OOO No. 2 [S. 145; R. 151]................	7.6– 8.9(?)	(25)
74	m-nitrobenzene-azo-salicylic acid; Alizarin yellow GG [S. 48; R. 36].............................	c(?) 10.0–12.0 y	(20, 21)
75	p-nitrobenzene-azo-salicylic acid; Alizarin yellow R [S. 58; R. 40].	y 10.0–12.1 y	(32)
76	α-naphthylaminosulfonic acid-azo-β-naphthol; Red I [S. 161; R. 176].	10.5–12.1	(31, 32)
77	α-naphthalene-azo-β-naphthol-3,6-disulfonic acid; Bordeaux B [S. 112; R. 88]...............	p 10.5–12.5 o	(3a)
77a	Isonitrosoacetyl-p-amino-azobenzene.......................	see p. 583	(24)
78	p-benzenesulfonic acid-azo-resorcinol; Tropaeolin O [S. 143; R. 148].......................	y 11.1–12.7 o	(32)

TABLE 8—*Continued*

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Mono-azo compounds—*Continued*		
79	Benzene-azo-β-naphthol-6,8-disulfonic acid; Orange GG (S. 38; R. 27]	y 11.5–14.0 p	(3a)
80	Crocein?	p 12.0–14.0 v	(29)
80a	Isonitroso-p-toluazo-p-toluidine	see p. 583	(24)
81	Helianthin (Grübler)?	o 11.0–12.0 r	(3a)
82	Helianthin I?	o 11.0–13.0 r	(29)
83	Helianthin II?	y 13.0–14.0 v	(29)
84	Curcumein?	o 0.0– 1.0 y y 13.0–15.0 g	(29)
	Dis-azo compounds		
85	Ditolyl-disazo-bis-β-naphthylamine-6-sulfonic acid; Benzopurpurin B [S. 365; R. 450]	b 0.3– 1.0 v v 1.0– 5.0 y y 12.0–14.0 r	(29)
86	Ditolyl-disazo-bis-α-naphthylamine-4-sulfonic acid; Benzopurpurin 4B [S. 363; R. 448]	v 1.3– 4.0 r	(15)
87	Diphenyl-disazo-bis-α-naphthylamine-4-sulfonic acid; Congo red [S. 307; R. 370]	b 3.0– 5.0 r	(29)
88	Ditolyl-disazo-bis-α-naphthol-4-sulfonic acid; Azo blue [S. 377; R. 463]	v 10.5–11.5 p	(3a)
89	Curcumin W [probably Rowe, 364].	mid-point 7.3 mid-point 7.6	(28) (9)
	Triphenylmethane derivatives		
90	Methylated pararosaniline; Crystal violet [S. 516; R. 681]	g 0.0– 2.0 b	(3a)
91	p, p′-tetramethyldiamino-triphenylcarbinol; Malachite green [S. 495; R. 657]	y 0.0– 2.0 g b 11.5–14.0 f	(29)
92	Hofmann's violet; methylated rosanilines and pararosanilines [S. 514; R. 679]	g 0.0– 2.0 b	(3a)
93	Tetraethyl-diamino-triphenylcarbinol; Brilliant green [S. 499; R. 662]	y 0.0– 2.6 g	(3a)

TABLE 8—*Continued*

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Triphenylmethane derivatives—*Continued*		
94	Heptamethylrosaniline; Iodine green [R. 686]..................	y 0.0– 2.6 b	(3a)
95	Hexaethylpararosaniline; Ethyl violet [S. 518; R. 682]..........	y 0.0– 3.6 b	(3a)
96	Ethyl-hexamethyl-pararosaniline; Ethyl green [R. 685]...........	y 0.3– 2.0 b	(15)
97	Methyl violet 6B; benzylated tetra- and pentamethyl-para-rosaniline [S. 517; R. 683].......	y 0.15– 3.2 v	(32)
98	Gentian violet; mixture..........	0.4– 2.7	(31, 32)
99	Aniline red; rosaniline and para-rosaniline [S. 512; R. 677].......	pu 1.2– 3.0 f	(3a)
99a	2,4,2′,4′,2″-pentamethoxytri-phenylcarbinol.................	v 1.2– 3.2 c	(16)
99b	2,4,2′,4′,2″,4″-hexamethoxytri-phenylcarbinol.................	p 2.6– 4.6 c	(16)
100	Red violet 5RS; di- and tri-sul-fonate of ethylrosaniline [S. 525; R. 693].........................	p 3.6– 6.0 c	(3a)
101	Resazurin [R. 727 note]..........	o 3.8– 6.5 v	(15)
102	China blue [S. 539; R. 707]; mix-ture...........................	b 4.7– 7.0 c	(3a)
102a	2,4,6,2′,4′,2″,4″-heptamethoxy-triphenyl carbinol..............	r 5.0– 7.0 c	(16)
103	Rosolic acid [S. 555; R. 724]; mix-ture...........................	br 6.9– 8.0 r	(32)
104	Alkali blue 4B [S. 536; R. 704]; mixture.......................	v 9.4–14.0 p	(3a)
105	XL soluble blue [S. 538; R. 706]; mixture.......................	b 10.0–13.0 p	(3a)
106	Poirrier's blue..................	b 11.0–13.0 r	(3a)
107	Acid fuchsin; di- and tri-sulfonic acids of rosaniline and para-rosaniline [S. 524; R. 692]......	r 12.0–14.0 f	(29)
	Phthaleins and related compounds (see also Thiel and Diehl, 1927)		
108	Diethyl-m-amino-phenolphtha-lein; Rhodamine B [S. 573; R. 749]...........................	o 0.1– 1.2 p	(3a)
109	Pyrogallol-phthalein; Galleïn [S. 599; R. 781]..................	variable 0–14	(29)

TABLE 8—*Continued*

INDEX NUM- BER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Phthaleins and related compounds—*Continued*		
110	Tetrabromofluorescein; Eosine Y S [S. 587; R. 768]............	y 0 – 3.0 fl	(3a)
111	Erythrosin (iodeosin); di- or tetra fluorescein [S. 591, 592? R. 772, 773?]..................	o 0.0– 3.6 fl	(3a)
112	Phloxin red B.H. (Grübler)?.....	p 1.4– 3.6 r	(3a)
113	Dihydroxyfluoran; Uranin (fluorescein) [S. 585; R. 766]........	y 3.6– 5.6 fl	(3a)
114	Dichlorofluorescein..............	y 4.0– 6.6 fl	(3a)
115	o-α-naphthol phthalein...........	y 8.9– 9.5g(f)	(8)
116	p-α-naphthol phthalein...........	y 7.0– 9.0 b	(32)
117	Tetrabromophenol phthalein	c 8.0– 9.0 v	(25)
118	o-cresoltetrachlorophthalein......	c 8.5– 9.0 pu	(1, 14)
119	o-cresolphthalein................	c 8.2– 9.8 r	(3b)
120	Phenolphthalein [R. 764]........	c 8.3–10.0 r	(20, 21, 32) .
120a	Dibromothymoltetrachloro- phthalein......................	c 8.4– 8.8 b	(7)
121	* 1,2,3-xylenolphthalein..........	c 8.9–10.2 b	(8)
121a	Thymoltetrachlorophthalein......	c 9.2–10.0 b	(7)
122	Thymolphthalein.................	c 9.3–10.5b(f)	(32)
123	Dibromo-dinitrofluorescein; Eosin BN [S. 590; R. 771]...........	p 10.5–14.0 y	(3a)
124	R=SCH₃ ⬡ OH	c 8.4–10.0 v	(12)
125	R=SC₄H₉ —C— OH	c 8.6– 9.8 v	(12)
126	R=SC₆H₅ O = C—O R	c 9.0–10.0 v	(12)
	Sulfonphthaleins		
127	Catecholsulfonphthalein..........	p 0.2– 0.8 o y 4.0– 7.0 g v 8.5–10.2 b	(22)
128	m-cresolsulfonphthalein; Meta-cresol purple..................	r 1.2– 2.8 y y 7.4– 9.0 pu	(5)
129	Thymolsulfonphthalein; Thymol blue.........................	r 1.2– 2.8 y y 8.0– 9.6 b	(3b)
130	Tetranitrophenolsulfonphthalein .	y 2.8– 3.8 r	(3b)
131	Tetrabromophenolsulfonphthalein; Bromphenol blue..........	y 3.0– 4.6 b	(3b)
132	* Tetrachlorophenolsulfonphthalein............................	y 3.0– 4.6 b	(3b)

TABLE 8—*Continued*

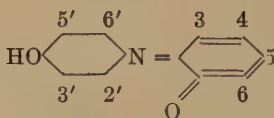| INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Sulfonphthaleins—*Continued*		
133	* Dichloro-dibromo-phenol-sul-fonphthalein; Brom-chlorphenol blue..........................	y 3.0– 4.6 b	(5)
134	Tetrabromo-m-cresolsulfon-phthalein; Bromcresol green....	y 3.8– 5.4 b	(5)
134a	Tetrachloro-m-cresolsulfon-phthalein......................	y 4.0– 5.6 b	(5)
135	Dichlorophenolsulfonphthalein; Chlorphenol red..............	y 4.8- 6.4 r	(5)
136	Dibromo-*o*-cresolsulfonphthalein; Bromcresol purple..............	y 5.2– 6.8 pu	(3b)
137	Dibromophenolsulfonphthalein; Bromphenol red	y 5.2– 6.8 r	(5)
138	* Diiodophenolsulfonphthalein ...	y 5.7– 7.3 pu	(3a)
139	Dibromothymolsulfonphthalein; Bromthymol blue..............	y 6.0– 7.6 b	(3b)
140	* Brom xylenol blue, dibrom-inated No. 145.................	y 6.0– 7.6 b	(5)
141	Phenol-nitrosulfonphthalein......	y 6.6 8.4 pu	(3b)
142	Phenolsulfonphthalein; Phenol red...........................	y 6.8– 8.4 r	(3b)
143	o-cresolsulfonphthalein; Cresol red	y 7.2– 8.8 r	(3b)
144	Salicylsulfonphthalein............	y 7.2– 9.2 p	(3a)
145	* 1.4-dimethyl-5-hydroxyben-zenesulfonphthalein; Xylenol blue...........................	y 8.0– 9.6 b	(4)
146	α-naphtholsulfonphthalein........	y 7.5– 9.0 b	(3b)
147	Carvacrolsulfonphthalein.........	y 7.8– 9.6 b	(3b)
148	Orcinsulfonphthalein.............	y 8.6–10.0 fl	(3b)
149	Nitro-thymolsulfonphthalein.....	v 9.2–11.5 y	(3b)
	Quinoline compounds		
150	α-(p-dimethylaminophenylethyl-ene)-quinoline ethiodide; Quin-aldine red. Eastman Kodak Co. No. 1361...................	1.0-2.0	(18)
150a	Pinacyanol [R. 808].............	pK = 3.7	(10, 18)
150b	Ortho-chrom-T [R. 807].........	pK = 6.7	(10, 18)
151	Quinoline blue (cyanin); 1,1′ di-iso-amyl-4,4′-quinocyanine iodide [S. 611; R. 806].........	c 7.0– 8.0 v	(31, 32)

TABLE 8—*Continued*

Index no. 152   Indophenols (6)

Color changes: from brownish or clear red in acid to deep blue in alkali.
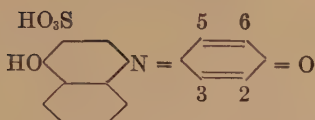All indophenols are somewhat unstable

$$HO\langle \quad \rangle N = \langle \quad \rangle = O$$

5' 6'   5 6
3' 2'   3 2
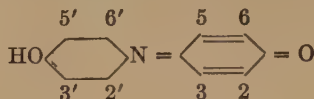
Indophenol

SUBSTITUENTS	pK
2,6,3' tribromo-...	5.1
2,6-dibromo-3'-chloro-......................................	5.4
2,6-dibromo-3'-methyl-......................................	5.4
2,6-dichloro-3'-chloro-......................................	5.8
2,6-dichloro-3'-methyl-......................................	5.5
2,6-dibromo-3'-methoxy-.....................................	5.6
2,6-dichloro-..	5.7
2,6-dibromo-..	5.7
2,6-dibromo-2'-methyl-......................................	5.9
2,6-dibromo-2'-bromo-......................................	6.3
2-chloro-..	7.0
2-bromo-..	7.1
3-bromo-..	7.8
Indophenol..	8.1
2-methyl-...	8.4
3-methyl-...	8.6
2-methoxy-..	8.7
2-isopropyl-5-methyl-......................................	8.8
2-methyl-5-isopropyl.......................................	8.9

5' 6'   3 4
3' 2'   6
O

$$HO\langle \quad \rangle N = \langle \quad \rangle 5$$

Orthoindophenol

SUBSTITUENTS	pK
3' bromo-...	7.1
Orthoindophenol..	8.4
2'-methyl-...	8.8

TABLE 8—*Continued*

$$\text{HO}_3\text{S} \quad \underset{3 \quad 2}{\overset{5 \quad 6}{\text{HO} \langle \quad \rangle \text{N} = \langle \overline{\overline{\quad\quad}} \rangle = \text{O}}}$$

Indonaphthol-3′-sulfonic acid

SUBSTITUENTS	pK
2,6 dichloro-...	6.1
Indonaphthol-3′-sulfonic acid	8.7
2-methyl-...	9.0

INDEX NUM-BER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Azines		
153	Safranine (which?)................	b−0.3− 1.0 r	(29)
154	Amino-dimethylamino-phenyl-diphenazonium chloride; Methylene violet B.N. [S. 680; R. 842]...........................	pu 0.0− 1.2 v	(3a)
155	Amino-phenylamino-p-tolyl-ditol-azonium sulphate; Mauve [S. 688; R. 846].....................	0.1− 2.9	(32)
156	Magdala red; mixture amino- and diamino-naphthyl-dinaphth-azonium chlorides [S. 694; R. 857]	p 3.0− 4.0 fl	(29)
157	Induline, spirit soluble [S. 697; R. 860]; mixture	b 5.6− 7.0 v	(3a)
158	Amino-dimethylamino-toluphen-azonium chloride; Neutral red [S. 670; R. 825].................	r 6.8− 8.0 y	(32)
159	Dimethylamino-phenyl-naphtho-phenazonium chloride; Neutral blue [S. 676; R. 832]...........	9.3−10.2	(31, 32)
	Oxazine compounds		
160	Dihydroxy-dinaphthazoxonium sulfonate; Alizarin green B [S. 657; R. 918]...................	v−0.3− 1.0 p / y 12.0−14.0 br	(33)
161	Diethylamino-benzylamino-naphtho-phenazoxonium chloride; Nile blue 2B [S. 654; R. 914].	b 7.2− 8.6 p	(3a)
162	Diethylamino-aminonaphtho-phenazoxonium sulfate; Nile blue A [S. 653; R. 913]...........	b 10.2−13.0 p	(3a)

TABLE 8—*Continued*

INDEX NUMBER	INDICATOR	COLOR AND USEFUL RANGE pH	LITERATURE
	Anthraquinones		
163	1,2-dihydroxy-anthraquinone-β-quinoline; Alizarin blue ABI [S. 803; R. 1066]...............	p 0.0– 1.6 y y 6.0– 7.6 g	(3a)
164	1,2,4-trihydroxy-anthraquinone; Purpurin [S. 783; R. 1037]......	y 0.0– 4.0 o o 4.0– 8.0 p	(3a)
165	Alizarin sulfonic acid; Alizarin red S [S. 780; R. 1034].........	y 3.7– 4.2 p	(36)
166	1,2-dihydroxy-anthraquinone; Alizarin [S. 778; R. 1027].	y 5.5– 6.8 r v 10.1–12.1 pu	(31, 32)
167	Alizarin blue S..................	various 6–14	(25)
	Indigos		
168	Indigo disulfonate; Indigo carmine [S. 877; R. 1180]...............	b 11.6–14.0 y	(3a)
	Miscellaneous and natural indicators		
169	Echtrot?.......................	y 0 – 1.0 r	(29)
170	Logwood [S. 938; R. 1246]........	various 0–14	(25)
171	* Red cabbage extract............	r 2.4–4.5 g	(35)
171a	Blue cabbage extract.............	various 2–11	(19)
172	1-oxynaphtho-quinomethane; Nierenstein's indicator.........	c 2.7– 3.7 pu	(36)
173	Tröger and Hille's indicator, $C_{14}H_{15}N_4SO_3H$..............	o 2.8– 3.9 y	(36)
174	Phenacetolin....................	y 3.0– 6.0 r r 10.0–13.0 c	(25)
175	Lacmosol......................	r 4.4– 5.5 b	(13)
176	Lacmoid [R. 908 note]............	r 4.4– 6.2 b	(31, 32)
177	Azolitmin (litmus) [R. 1242]......	r 4.5– 8.3 b	(31, 32)
178	Cochineal [S. 932; R. 1239].......	y 4.8– 6.2 v	(31, 32)
179	Archil (orchil) [S. 934; R. 1242]...	p 5.6– 7.6 v	(3a)
180	Brazilein [S. 935; R. 1243]........	c 6.0– 8.0 p	(3a)
181	Di-o-hydroxy-styryl ketone; Lygosine......................	y 7.3– 8.7 g	(36)
182	Mimosa flower extract...........	7.7– 9.6	(32)
183	Turmeric (curcuma) [S. 927; R. 1238]........................	y 7.8– 9.2 br	(15)
184	Alkannin [R. 1240, note] cf. alizarin......................	8.3–10.0	(31, 32)
185	α-naphtholbenzein...............	y 8.5– 9.8 g	(31, 32)

TABLE 8—*Concluded*

(1) Arnold (1924).
(2) Bogert and Scatchard (1916).
(3a) Clark, Cohen and Elvove (see text, page 71).
(3b) Clark and Lubs (1915–1917).
(4) Cohen, A. (1923).
(5) Cohen, B. (1927).
(6) Cohen, Gibbs and Clark (1924).
(7) Cornwell and Esselstyn (1927).
(8) Csányi (1921).
(9) Fels (1904).
(10) Hegge (1925).
(11) Henderson and Forbes (1910).
(12) Holt and Reid (1924).
(13) Hottinger (1914).
(14) Hundley and McClendon (1925).
(15) Kolthoff (1923).
(16) Kolthoff (1927).
(17) Laxton, Prideaux and Radford (1925).

(18) McClendon (1924).
(19) Milobedzki and Jajte (1926).
(20) Michaelis and Gyemant (1920).
(21) Michaelis and Krüger (1921).
(22) Moir (1920).
(23) Moir (1923).
(24) Naegeli (1926).
(25) Prideaux (1917).
(26) Prideaux (1924).
(27) Rowe (1924).
(28) Salessky (1904).
(29) Salm (1906).
(30) Schultz (1923).
(31) Sørensen (1909).
(32) Sørensen (1912).
(33) Thiel Dassler and Wülfkin (1924).
(34) Thiel and Wülfkin (1924).
(35) Walbum (1913).
(36) Walpole (1914).

TABLE 9

Common synonyms of indicators

Among synonyms given in this table are several which apply to dyes which are not listed in preceding table or which have been applied to two or more of the indicators listed. Such cases are indicated by*. Numbers are index numbers of table 8.

Acid bordeaux, 77
Acid brown R,* 68
Acid fuchsin,* 107
Acid magenta II, 107
Acid roseine, 107
Alizarin, 166
Alizarin blue ABI, 163
Alizarin blue S, 167
Alizarin blue X, 163
Alizarin carmine, 165
Alizarin green B, 160
Alizarin red S, 165
Alizarin sulfonate or S, 165
Alizarin yellow GG, 74
Alizarin yellow R, 75
Alkali blue 4B, 104

Alkanet, 184
Alkalin, Alkannin, 184
Alphanaphtholbenzein, 185
Alphanaphtholphthalein,* 116
Amido-azo-benzol, 30
Amido-azo-toluol, 26
Amino-azo-benzene, 30
Amino-azo-toluene, 26
Amyl red, 66
Anchusin, 184
Aniline orange,* 31
Aniline red, 99
Aniline yellow,* 3, 25, 30
Archil, 179
Aurin, 103
Azo-blue, 88

TABLE 9—*Continued*

Azolitmin, 177
Azoresorcin, 101
Benzopurpurin B, 85
Benzopurpurin 4B, 86
Benzyl violet, 97
Beta naphthol orange, 73
Bitter almond oil green, 91
Blauholz, 170
Boettger's indicator, 184
Bordeaux B, 77
Brasilein, brasilin, brazilin, 180
Brazil wood, 180
Brilliant green, 93
Brilliant yellow,* 89
Brom-chlor-phenol blue, 133
Brom cresol green, 134
Brom cresol purple, 136
Brom phenol blue, 131
Brom phenol red, 137
Brom thymol blue, 139
Brom xylenol blue, 140
Butter yellow,* 26, 37
Cabbage red, 171
Campeachy wood, 170
Carmine, 178
Carminic acid, 178
Catechol sulphonphthalein, 127
China blue, 102
Chlor phenol red, 135
Chrome printing orange R, 75
Chrome printing yellow G, 74
Chrysoidine,* 56
Chrysoine, 78
Coccus, 178
Cochenille, cochineal, 178
Congo, 87
Congo red, 87
Corallin, 103
Cresol red, 143
Cresolphthalein,* 119
Cresolsulphonphthalein,* 143
Crismer's indicator, 101
Crocein,* 80
Crystal violet, 90

Curcuma, 183
Curcumein,* 84
Curcumin,* 183
Curcumin W, 89
Curcummin,* 183
Cyanin, 151
Dechan's indicator, 109
Degener's indicator, 174
Dianil red,* 87
Dichlorofluorescein, 114
Diethylaniline orange, 45
Dihydroxyanthraquinone, 166
Dimethylaniline orange, 44
Dimethyl orange, 44
Dimethyl yellow, 37
Dinitroaminophenol, 9
Dinitrohydroquinone, 5
Echtrot,* 169
Echtrot A, 76
Echtrot B, 77
Eosine, 110
Eosine BN, 123
Eosine YS, 110
Erythrosine,* 111
Ethyl green,* 96
Ethyl orange, 45
Ethyl red,* 60
Ethyl violet, 95
Fast red A, 76
Fast red B,* 77
Fluorescein, 113
Formanek's indicator, 160
Fuchsia, 154
Fuchsin,* 99
Fuchsin S, 107
Galeine, 109
Gallein, 109
Gentian violet, 98
Golden orange, 44
Haematein,*[1] 170
Haematoxylin,*[1]   haematoxylon,*
    170
Helianthine,* 44, 81, 82, 83
Hematein,*[1] hematine,*[1] 170

[1] Haematoxylin is the leuco-compound of Haematein or Hematine as obtained from logwood although the name is sometimes given to the oxidized form. Haematein or Hematine should not be confused with Hematin of the blood pigment.

TABLE 9—*Continued*

TABLE 9—*Concluded*

Phloxin red BH, 112
Phosphine substitute, 78
Picric acid, 1
Pinacyanol, 150a
Poirrier's blue C4B, 106
Poirrier's orange III, 44
Propyl red, 61
Purpurin, 164
Pyrogallol phthalein, 109
Quinaldine red, 150
Quinoline blue, 151
Red I, 76
Red cabbage extract, 171
Red violet 5R,* 92
Red violet 5RS, 100
Red wood, 180
Resazurin, 101
Resorcin blue,* 176
Resorcin phthalein, 113
Resorcin yellow, 78
Rhodamine B, 108
Riegel's indicator, 87
Rosaniline, 99
Roseine, 99
Rose magdala, 156
Rosolane, 155
Rosolic acid, 103
Rotholz, 180
Rubine S, 107
Safranine,* 153
Salicyl yellow,* 74
Schaal's indicator, 166
Soluble blue 3M, 2R, 102
Soluble red woods, 180
Spirit yellow, 30

Spirit yellow G, 30
Spirit yellow R, 26
Tetra brom fluorescein, 110
T. N. T. 18
Thymol blue, 129
Thymolphthalein, 122
Toluidine orange* (ortho), 39
Toluidine orange* (meta), 47
Toluylene red,* 158
Töpfer's reagent, 37
Tournesol, 177
Tröger and Hille's indicator, 173
Tropaeolin*,? 69
Tropaeolin D, 44
Tropaeolin G,* 23, 72
Tropaeolin O, 78
Tropaeolin OO, 25
Tropaeolin OOO No. 1, 72
Tropaeolin OOO No. 2, 73
Tropaeolin R, 7
Turmeric, 183
Turnsole, 177
Uranin, 113
von Müller's indicator?, 25
Weselsky's indicator, 101
Water blue, 102
XL Soluble blue, 105
Xylenol blue, 145
Xylenol phthalein,* 121
Xylidine orange* (meta), 40
Xylidine orange* (para), 48
Yellow B, 37
Yellow T, 78
Zellner's indicator, 113

SELECTED INDICATORS

Table 10 is Sørensen's list. Concerning these indicators Sørensen remarks:

Not all these indicators furnish equally well defined *virages* and above all they are not of equal applicability under all circumstances. In the choice of an indicator from among those which we have been led to recommend it is necessary to use judicious care and especially to take into consideration the following facts:

a. The indicators of the methyl violet group (nos. 1 and 2) (see table 10) are especially sensitive to the action of neutral salts; furthermore the intensity of color changes on standing and the change is the more rapid the more acid the medium.

b. The basic indicators (nos. 3, 6, 9, 11, 14) are soluble in toluene and in chloroform. The first four separate partially on prolonged standing of the experimental solution.

c. In the presence of high percentages of natural proteins most of the indicators are useless although certain of them are still serviceable; nos. 1, 2, 13, 16, 17, 18.

d. In the presence of protein decomposition products even in considerable proportions the entire series of indicators may render real service. Yet even in these conditions some of the acid azo indicators may give notable errors (nos. 4, 5, 7, 8, 10) in which case one should resort to the corresponding basic indicators.

e. When only small percentages of protein or their decomposition products are concerned the acid azo indicators are more often preferable to the basic for they are not influenced by toluene or chloroform and do not separate from solution on standing.

f. In all doubtful cases—for example in the colorimetric measurement of solutions whose manner of reaction with the indicator is not known, the electrometric measurement as a standard method should be used. Then the worth of the indicator will be determined by electrometric measurement with colorimetric comparison.

In table 11 will be found the selection of Clark and Lubs, modified by the rejection of methyl red and the inclusion of Cohen's contributions. These indicators are marketed both in the form of the dry powder and in stock solutions. In cases where the acidity of the free acid dye does not interfere with accuracy and when alcohol is not objectionable the alcoholic solutions of the dyes may be used. Clark and Lubs prefer to use aqueous solutions of the alkali salts in concentrations which may be conveniently kept as stock solutions. These are diluted for the test solutions used in the dropping bottles.

For the preparation of these stock solutions one decigram (0.1 gram) of the dry powder is ground in an agate mortar with the quantities of NaOH shown in column A and footnote in table 11.

If there be no particular reason to maintain exact equivalents it may be found easier to dissolve the dyes in 1.1 equivalents of alkali instead of one equivalent as indicated above. See page 190.

To place the dyes upon a comparable basis the final dilution should be nearly the same when calculated upon a molar basis

TABLE 10
Sørensen's Selection of Indicators

	Sørensen's Number	Index Number	Composition of Test Solution	Useful Range pH	Sensitivity to Neutral Salts	Usefulness in Presence of — True proteins	High conc. of products of proteolysis	Chloroform and toluene	Stability on Standing
Methyl violet 6B	1	97	0.01–0.05 per cent aqueous	y 0.1– 3.2 v	high	fair	good	with chloroform not, with toluene useful	acid solutions fade
Mauve	2	155	0.01–0.05 per cent aqueous	0.1– 2.9	high	fair	good	as above	as above
Benzene-azo-diphenylamine	3	22	0.01 gram in 1 cc. N HCl + 50 cc. alcohol + 49 cc. water	p 1.2– 2.1 y	low	not	fair	not	moderate
Tropaeolin OO	4	25	0.01 per cent aqueous	r 1.4– 2.6 y	low	not	fair	good	good
Metanil yellow	5	23	0.01 per cent aqueous	r 1.2– 2.3 y	low	not	fair	good	good
Benzene-azo-benzylaniline	6	34	0.02 gram in 1 cc. N/10 HCl + 50 cc. alcohol + 49 cc. water	p 2.3– 3.3 y	low	not	good	not	moderate
p-benzenesulfonic acid-azo-benzylaniline	7	32	0.01 per cent aqueous	r 1.9– 3.3 y	low	not	fair	good	good
p-benzenesulfonic acid-azo-m-chlorodiethylaniline	8	35	0.01 per cent aqueous	r 2.6– 4.0 y	low	not	fair	good	good
Benzene-azo-dimethylaniline	9	37	0.01 gram 0.1 cc. N/10 HCl + 80 cc. alcohol + 20 cc. water	r 2.9– 4.0 y	low	not	good	not	moderate
Methyl orange	10	44	0.01 per cent aqueous	r 3.1– 4.4* y	low	not	fair	good	good
Benzene-azo-α-naphthylamine	11	53	0.01 gram in 0.4 cc. N/10 HCl + 30 cc. alcohol + 70 cc. water	r 3.7– 5.0 y	low	not	good	not	moderate

p-benzenesulfonic acid-azo-α-naphthylamine	12	50	0.01 gram in 60 cc. alcohol + 40 cc. water	r 3.5- 5.7 y	low	not	good	good	good
Methyl red	12a	59	0.02 gram in 60 cc. alcohol + 40 cc. water	r 4.2- 6.3* y	low	S.C.	good	good	moderate
p-nitrophenol	13	12	0.04 gram in 6 cc. alcohol + 94 cc. water	c 5.0- 7.0* y	moderate	good	good	good	good
Neutral red	14	158	0.01 gram in 50 cc. alcohol + 50 cc. water	r 6.8- 8.0* y	low	S.C.	good	S.C.	good
Rosolic acid	15	103	0.04 gram in 40 cc. alcohol + 60 cc. water	br 6.9- 8.0 r	low	fair	good	fair	good
Tropaeolin OOO no. 1	16	72	0.01 per cent aqueous	v 7.6- 8.9 p	low	good	good	good	good
p-α-naphtholphthalein	16a	116	0.1 gram in 150 cc. alcohol + 100 cc. water	y 7.3- 8.7 b	moderate	S.C.	good	good	fair
Phenolphthalein	17	120	0.05 gram in 50 cc. alcohol + 50 cc. water	c 8.3-10.0* r	moderate	S.C.	good	good	good—fades in strong alkali
Thymolphthalein	18	122	0.04 gram in 50 cc. alcohol + 50 cc. water	c 9.3-10.5 b	moderate	S.C.	good	good	fades in moderate alkali
Alizarin yellow R	19	75	0.01 per cent aqueous	y 10.1-12.1 v			good	good	good
Tropaeolin O	20	78	0.01 per cent aqueous	y 11.1-12.7 o			fair		good

S.C. = useful in special cases. b = blue; br = brown; o = colorless; o = orange; p = pink; r = red; v = violet; y = yellow.

* Apparent pK values referred to standard buffers: Methyl orange (44), 3.7. Methyl red (59), see table 13. Paranitrophenol (12), see table 19. Neutral red (158), 6.85. Phenolphthalein, see table 13.

TABLE 11

Indicators selected by Clark and Lubs (1917)* supplemented by Cohen (1927)†

COMMON NAME	MOLECULAR WEIGHT	A	pK	RANGE	COLOR CHANGE ACID → ALKALINE	B	C	ABSORPTION MAXIMUM	
				pH		pH	pH	Acid $m\mu$	Alk. $m\mu$
Meta cresol purple†	382	26.2	1.51‡	1.2–2.8	red-yellow	conc. HCl	6	533	
Thymol blue*	466	21.5	1.5‡	1.2–2.8	red-yellow	conc. HCl	6	544	
Brom phenol blue*	669	14.9	3.98	3.0–4.6	yellow-blue	0	7		592
Brom cresol green†	698	14.3	4.67	3.8–5.4	yellow-blue	1	8		617
Chlor phenol red†	423	23.6	5.98	4.8–6.4	yellow-red	2	9		573
Brom phenol red†	512	19.5	6.16	5.2–6.8	yellow-red	3	10		574
Brom cresol purple*	540	18.5	6.3	5.2–6.8	yellow-purple	3	10		591
Brom thymol blue*	624	16.0	7.0	6.0–7.6	yellow-blue	4	10		617
Phenol red*	354	28.2	7.9	6.8–8.4	yellow-red	5	11		558
Cresol red*	382	26.2	8.3	7.2–8.8	yellow-red	5	11		572
Meta cresol purple†	382	26.2	8.32	7.4–9.0	yellow-purple	5	11		580
Thymol blue*	466	21.5	8.9	8.0–9.6	yellow-blue	6	12		596
Cresol phthalein*	—	—	[9.4]	8.2–9.6	colorless-red	6	12		—

A = cubic centimeters of 0.01 N NaOH required per 0.1 gram indicator to form mono sodium salt. Dilute to 250 cc. for 0.04 per cent reagent.

B = approximate pH value of solution required for full "acid color" appertaining to pH range indicated.

C = approximate pH value of solution required for full "alkaline color" appertaining to pH range indicated.

‡ Data by Holmes and Snyder (1925). It is not clear whether they used Clark and Lubs' (1916) preliminary data for HCl-KCl mixtures in calculations for which a large Bjerrum extrapolation was employed, or their own measurements, and, if their own, what basis of calculation was employed. See page 202 and footnote, page 478.

and, by reason of the great change in molecular weight caused
by the introduction of bromine and other group substituents,
equal molecular concentrations will be very far apart in per-
centage concentration. For all ordinary purposes, however, this
may be neglected and solutions of a concentration of 0.04 per
cent will be found satisfactory for use in testing 10 cc. of a solu-
tion with about five drops of indicator.

From various sources have come complaints that the method
outlined above for the preparation of the aqueous alkali salt
solution of brom cresol purple[1] leads to a solution of much lower
tinctorial power than when the same material is taken up directly
in alcohol. No such difficulty was experienced with the material
described by Lubs and Clark but it has appeared not infrequently
since. The source of the difficulty is not yet definitely traced,
but is suspected to be due to impurities. If so it should be
avoided by purchasing the highly purified material which is now
made specially.

Since the range of an indicator depends to a considerable extent
upon the manner in which the indicator is used, it is of interest
to note the ranges assigned by Saunders (1923) on the basis of
his ability to detect changes of 0.02 pH unit.

Brom cresol purple.................................... 5.8 –6.4
Brom thymol blue..................................... 6.4 –7.2
Phenol red... 7.1 –7.9
Cresol red... 7.65–8.45
Thymol blue... 8.4 –9.2

Phenolphthalein, or orthocresolphthalein, and methyl red,
which are valuable indicators for titrations, may be used for this
purpose in alcoholic solution unless exacting requirements are to
be met.

Since the requirements of titration are so varied no separate
lists for this process have been compiled. The theory of titration
is outlined in Chapter XXVIII. There reference will be made to
the color chart (page 65) for the selection of various end-point

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[1] The effect of excess alkali on sulfonphthaleins is still more or less
uncertain. See, however, Hubbard and Meeker (1924), Brown (1923),
Brightman, Hopfield and Meacham and Acree (1918). Also search the papers
of Orndorff.

colors to be used in conjunction with figures 93 and 94 (page 535). There, also, reference is made to the indicator constants of table 11 which are used for more refined work.

Michaelis' selection of "one-color" indicators is given in table 12. Discussion will be found in Chapter VI.

TABLE 12

Michaelis' indicators and their ranges as used in the method of Michaelis and Gyemant (see Chapter VI)

Picric acid.....................................	colorless	0.0– 1.3 yellow
2, 4-dinitro phenol.............................	colorless	2.0– 4.7 yellow
α dinitro phenol		
2, 6-dinitro phenol.............................	colorless	1.7– 4.4 yellow
β dinitro phenol		
2, 5-dinitro phenol.............................	colorless	4.0– 6.0 yellow
γ-dinitro phenol		
m-nitro phenol.................................	colorless	6.3– 9.0 yellow
p-nitro phenol.................................	colorless	4.7– 7.9 yellow
Phenolphthalein................................	colorless	8.5–10.5 red
Alizarin yellow GG.............................	colorless	10.0–12.0 yellow
Salicyl yellow		

MIXED INDICATORS

Mixtures of indicators are used for two purposes. The modification of color is discussed in Chapter VII. In that chapter will be found, in terms of absorption spectra, an example of the resultant effect of pH-change upon the simultaneous changes in degree of dissociation of each component. The more usual purpose of a mixture is to extend the pH range which can be covered by one test solution.

In one sense indicator mixtures are comparable with those indicators which have several ionizations each associated with a color change. Henderson and Forbes' (1910) employment of dinitrohydroquinone provided one of the earlier instances in which use was made of a compound of several stages of dissociation. With this one indicator they were able to cover roughly the range pH 3 to pH 9.

Prideaux and Ward (1924) describe the "universal indicator"

put out by the British Drug Houses as having the following color changes:

pH..........................	4.2	4.8	5.4	6.8
color.......................	red	yellow-ish red	orange yellow	yellowish green

pH..........................	7.3	9.1	10.3	11.5
color.......................	sap green	greenish blue	violet	reddish violet

Bogen (1927) describes a mixture with a range of from pH 1 to pH 10. His receipt is as follows.

Phenolphthalein, 100 mgm.; methyl red, 200 mgm.; dimethylaminoazo-benzene, 300 mgm.; bromthymol blue, 400 mgm.; thymol blue, 500 mgm. Dissolve in 500 cc. of absolute alcohol. Add tenth normal sodium hydroxide solution until the red disappears and the solution becomes yellow (pH 6.0).

The colors produced resemble those of the spectrum, thus:

Red	indicates about pH	2.0	(very strongly acid)
Orange	indicates about pH	4.0	(strongly acid)
Yellow	indicates about pH	6.0	(weakly acid)
Green	indicates about pH	8.0	(weakly alkaline)
Blue	indicates about pH	10.0	(strongly alkaline)

Moir (1917) is cited as using a mixture of methyl red, naphthol phthalein and phenolphthalein. To this Carr (1922) adds brom thymol blue or cresol phthalein, or cresol red.

Niklas and Hock (1924) are cited as employing the following mixture: one volume 0.04 per cent brom cresol purple, 4 volumes 0.04 per cent brom phenol blue, 6 volumes 0.02 per cent methyl red and 4 volumes 0.04 per cent brom thymol blue. Range pH 3.5 to 7.6.

Felton (1921) used equal parts of methyl red and brom thymol blue for the range 4.6 to 7.6 (unsatisfactory between 5.6 and 6.2); methyl red and brom cresol purple 4.6 to 7.0; methyl red and thymol blue (rough) 1.2 to 9.0.

Lizius and Evers (1922) cite the following:

ARBITRARY NAME	COMPONENTS	pH RANGE	COLOR
Methyl-thymol blue	Methyl red (1 part), thymol blue (3 parts)	4–10	red-yellow-greenish blue
Phenol violet	Phenolphthalein (1 part), thymol blue (6 parts)	8–10	yellow-blue-violet
Phenol-thymol phthalein	Phenol phthalein (1 part), thymol phthalein (6 parts)	8.3–11	Colorless-pink-violet
Thymol violet	Tropaeolin O (1 part), thymolphthalein (4 parts)	9–13	Yellow-green-blue-violet

See also A. Cohen (1922), Lizius (1921) and Kolthoff (1927) on mixed indicators.

INORGANIC INDICATORS

Grünberg (1924) notes that complex platinum compounds behave as acid-base indicators. A number of other inorganic systems have been used either as involving a species precipitated within a certain zone of pH or as involving a color change. See Houben (1919), Daniel (1927).

CHAPTER V

Theory of Indicators

It requires a long-necked observer to see the whole firmament out of one window.—J. Arthur Thomson.

INTRODUCTION

Indicator theory is a cross-roads. Here the organic chemist fetches structural formulas, group names, and correlations between molecular architecture and "color." The physicist brings his account of the radiant energy absorbed, methods for its measurement, and schemes for its translation into color. The psychologist pauses here to philosophize on color and to reflect upon the eye as a differentiating instrument. The physical chemist has called the cross-roads his own for he has tried to bridge the gap between the knowledge supplied by chemistry and that supplied by physics; but his sole outstanding contribution has been to formulate what can be formulated by equilibrium equations. The colloid chemist has occasionally tried to direct the traffic. He possesses valuable information the submission of which is welcomed as a service. The botanist has left on the roadside the historically important indicators and the entomologist has furnished cochineal. The bacteriologist has brought some of the first records of dye reduction and has asked of the plant physiologist what part acidity and what part reduction plays in the beauty of the autumn landscape. The analyst has camped here to acquire for his daily use the information that comes this way. And he who has imagined the chemistry to come, illustrated with electron orbits, seeks in the passing throng the bearer of the Rosetta stone that will translate speculative ideas concerning the electronic nature of organic reactions into reasonable certainties. Beside him stand the biochemist and pharmacologist, awaiting the formulation of what neither structural chemistry alone nor physical measurement alone seems to suggest half so well as the imagination which has been fired by the contributions of all. For the indicator has been shown to be a labile thing, responsive

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to radiant energy and to the pressures of protons and electrons, subject to structural changes and physical changes in delicate response to changes in the environment. It is the embodiment of sets of phenomena having an "all-togetherness" with which our intellectual methods have hardly attained the power to cope. The indicator reminds the biochemist of many things in the chemistry of life that exhibit an analogous "togetherness." He hopes that a complete mastery of indicator theory may take its part in the understanding of the unity and lability of life-chemistry.

But our present task is limited and commonplace. We must separate and assign to another chapter the physical phenomena of light absorption. We must relegate to the treatises on organic chemistry details of structure and the proofs thereof which the thoughtful student will require. We must pass over the fascinating story of indicator history with its contributions to theory. In short we must select only that which is essential to the use of indicators for the measurement of hydrion concentration. Hence there will be found in this chapter little of what is sometimes called indicator theory.

OSTWALD'S THEORY

Let us deal first with the simple theory of Ostwald which was constructed on the *primâ facie* evidence that indicators do behave as acids or bases, the molecules of which have abilities to absorb radiant energy of one spectral band, and the ions of which have abilities to absorb radiant energy of another spectral band.

If we start with this as a postulate, it is evident that the "color" of an indicator should change with the pH of a solution exactly as depicted by one of the dissociation curves described in Chapter I. If, for instance, the indicator is an acid, colorless in the undissociated form, but colored when dissociated as an anion, then the change of color with the hydrogen ion concentration should conform to the equation:

$$\alpha = \frac{K_a}{K_a + [H^+]} \tag{1}$$

where K_a is the dissociation constant of the acid indicator and α is the degree of dissociation. Assuming that such a relation

does hold, let us determine K_a for a series of indicators in the following way.

From the above equation when $\alpha = \frac{1}{2}$, $K_a = [H^+]$. That is, at a hydrogen ion concentration corresponding numerically to the dissociation constant, the acid is half dissociated. At such a hydrogen ion concentration a colorless-to-red indicator, such as phenolphthalein, should show half the available color; and a yellow-to-red indicator, such as phenol red, should show the half-yellow, half-red state. We can match the half-way state of this first solution by superimposing two solutions each of a depth equal to the first, if we have in one of the superimposed solutions only the yellow form and in the other only the red form, each concentration equaling half the concentration in the first solution. Such an arrangement is shown diagraphically in the following figure:
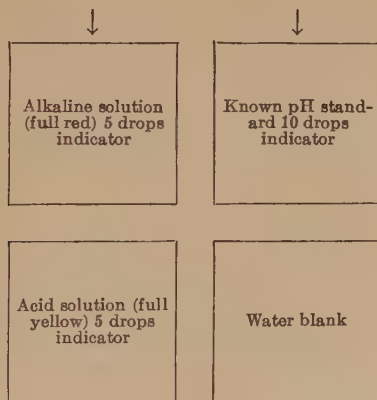
We may not know at the beginning at what pH the half transformation may occur, so we vary the pH of the standard solution until a match with our superimposed solutions does occur. Then we have found, presumably, the hydrogen ion concentration the numerical value of which is that of the dissociation constant of the indicator. Values so obtained by Clark and Lubs (1917) are given in table 13.

This is the method of Salm (1906).

Of course it is not necessary to confine attention to the case where each of the superimposed tubes at the left in the diagram

contains the same quantity of the indicator. Various divisions between the solutions inducing the full "alkaline color" and the full "acid color" may be made; and in each instance a color-match may be made by adjusting the standard buffer until the ratio of the "acid form" to the "alkaline form" is that of the artificial division between the acid and the alkaline solutions.

TABLE 13

Approximate apparent dissociation constants of indicators

INDICATOR	K_a	pK
Phenol sulfon phthalein.............................	1.2×10^{-8}	7.9
o-Cresol sulfon phthalein...........................	5.0×10^{-9}	8.3
Thymol sulfon phthalein............................	1.2×10^{-9}	8.9
Carvacrol sulfon phthalein..........................	1.0×10^{-9}	9.0
α-Naphthol sulfon phthalein.........................	5.3×10^{-9}	8.2
Tetra bromo phenol sulfon phthalein...............	7.9×10^{-5}	4.1
Di bromo o-cresol sulfon phthalein.................	5.0×10^{-7}	6.3
Di bromo thymol sulfon phthalein..................	1.0×10^{-7}	7.0
Phenol phthalein...................................	2.0×10^{-10}	9.7
o-Cresol phthalein.................................	4.0×10^{-10}	9.4
α-Naphthol phthalein..............................	4.0×10^{-9}	8.4
Methyl red..	7.9×10^{-6}	5.1
Ethyl red...	4.0×10^{-6}	5.4
Propyl red..	4.0×10^{-6}	5.4
Thymol sulfon phthalein (acid range)...............	2.0×10^{-2}	1.7

Thus it is possible to determine various values of α and, by means of equation (1) or (1a), to determine whether the simple require-

$$pH = pK + \log \frac{\alpha}{1 - \alpha} \tag{1a}$$

ments of the Ostwald theory are met *formally*. Figure 18 shows some examples. In this figure the experimental points are shown lying on or very near type curves drawn to correspond to equation (1a) and placed with reference to the pH axis by using the average value of pK calculated from the known pH-values of the buffers and the measured values of α.

As indicated in Chapter I the determination of the dissociation curve, or of the half transformation point, does not tell us whether we are dealing with the dissociation curve of an acid or the disso-

ciation-residue curve of a base or *vice versa*. Thus methyl red is treated in table 13 as an acid and plotted in figure 19 as if the color were associated with the undissociated form. Methyl red however could be treated as a base.

Figure 19 shows at a glance that an indicator of the simple type we have assumed has no appreciable dissociation and consequently exists in only one colored form at pH values beginning about 2 points below the half transformation point, while at the same distance above this point the indicator is completely dissociated and exists only in its second form. Between these limits the
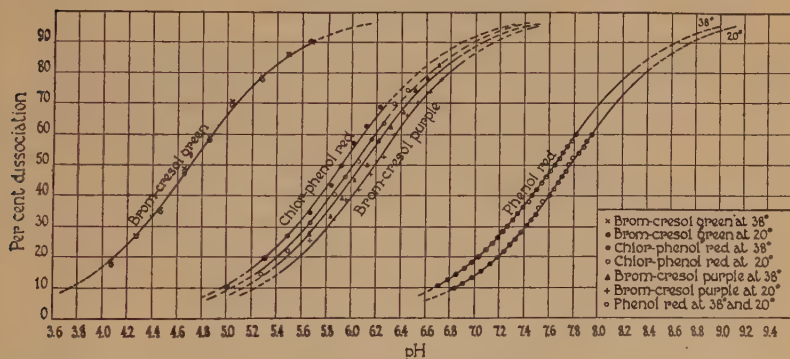
Fig. 18. Calculated and Observed Dissociation Curves for Indicators, Used in Urine pH Determination

(After Hastings, Sendroy and Robson (1925))

color changes may be observed. The useful range of such an indicator is far less than 4 pH units for optical reasons which will be discussed in Chapter VII.

The illustration (fig. 19) will show how in choosing a set of indicators it is advantageous to include a sufficient number, if reliable indicators can be found, so that their ranges overlap. It shows that each of the indicators, when considered to be of the simple type we have assumed, has an equal range. It also shows that the half transformation point of each indicator occurs nearer one end of the useful range, the useful range being indicated by the shaded part of the curve. This aspect will be discussed later.
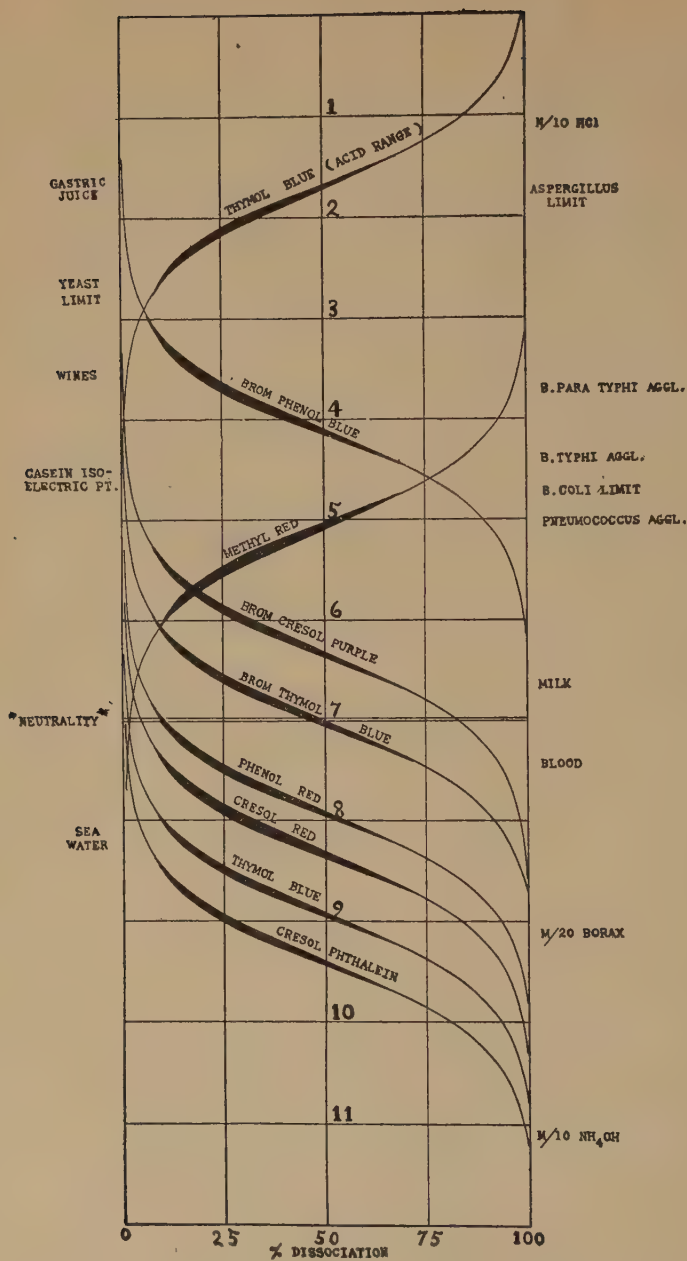
FIG. 19. INDICATOR CURVES AND SIGNIFICANT pH VALUES
Shading indicates useful range

104

It is evident that if the actual color change of an indicator varied with pH in accordance with a curve such as those in figure 19, and if the true dissociation constant were accurately known, then the hydrogen ion concentration of a solution could be determined by finding the per cent transformation induced in the indicator. Indeed the dissociation constants of some few indicators have been determined with sufficient accuracy to permit the use of this method when the proper means of determining the color intensities are used. This will be discussed in Chapters VI and VII.

TAUTOMERISM

The following sketch of tautomerism is purposely made brief. Its consideration leads to equations which reduce to the forms used with the Ostwald theory. Further consideration would lead to very many points of interest but these are involved in the use of indicators which are ordinarily rejected.

Without following the detail of the reasoning we may say that certain reactions of isatin suggest the formula

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
C_6H_4 \diagup \quad \diagdown C{=}O \\
\diagdown \text{N} \diagup \\
\text{H}
\end{array}
$$
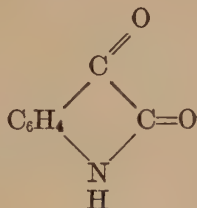
while other reactions of isatin suggest the formula

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
C_6H_4 \diagup \quad \diagdown C{-}OH \\
\diagdown \text{N} \diagup
\end{array}
$$
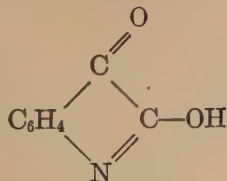
Since the study of this case there have been found many compounds which act now in one way and again in another, according to the conditions used and the reagents with which they are attacked. To account for a case like that of isatin it has been

assumed that a hydrogen atom moves from one position to the other, that the two forms are in dynamic equilibrium and that when a reagent attacks one form the other rearranges to maintain the dynamic equilibrium and thus maintain a supply of the reacting form.

Among the types are those with the lactam and lactim structures and those with the keto and enol structures.

$$\begin{array}{cccc} -C{=}O & -C{-}OH & -C{=}O & -C{-}OH \\ | & || & | & || \\ -NH & -N & -CH & -C{-} \\ & & | & \\ \text{Lactam} & \text{Lactim} & \text{Keto} & \text{Enol} \end{array}$$
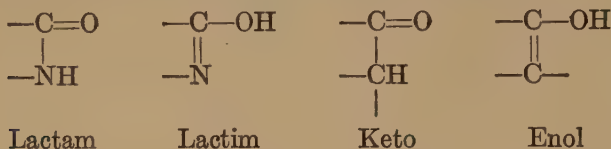
From one and the same compound have been formed derivatives corresponding to the enolic or to the ketonic structure. The two forms of the original substance are isomers; but to emphasize their labile nature Laar (1885) called them *tautomers*. To denote each and every shade of meaning in explanations which differ, we now find more terms than we can afford space to define. We shall use the word tautomerism to denote labile isomeric changes of whatever nature.

Frequently tautomeric rearrangements are associated with change of color. The argument is as follows. In those beautiful and often very elaborate series of syntheses by means of which the organic chemist attains an orderly view of structures, it is noted that color is associated with various, particular structures. When a colorless ionogen is converted into an ion, a colorless ion might be expected. But the fact that the ion is colored is the occasion for believing that a rearrangement takes place with the production of one or another of those structures which have been associated with color production. Groups which, by their presence, "produce" color are called chromophores. Important chromophores are:
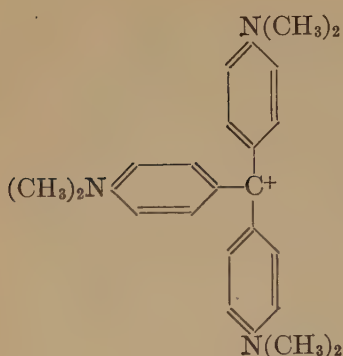
$$>C{=}O; >C{=}S; >C{=}N-; -NO; -NO_2; -N{=}N-; =\langle\!\!\!\bigcirc\!\!\!\rangle=$$

$$\text{and}=\langle\!\!\!\bigcirc\!\!\!\rangle$$
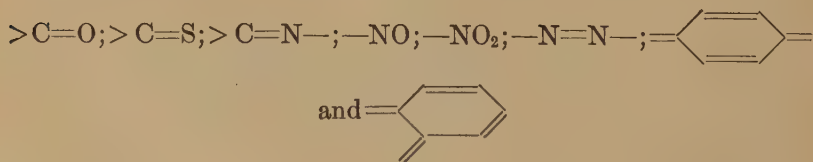
Of particular importance to our subject are groups such as
$-NH_2$, $-OH$, etc., which are not chromophores *per se* but which
may have a profound influence upon the calling forth or the
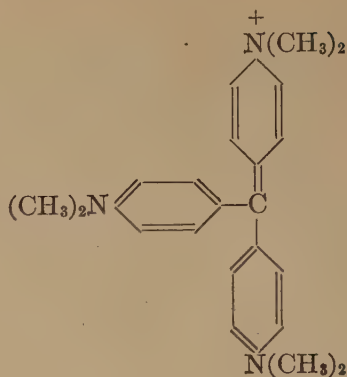suppression of the appearance of color.

Now consider the case of crystal violet. The "free base" will
be represented by formula I. It contains no chromophore. It
is colorless. However it contains substituted amino groups and
a hydroxyl group. Therefore it is an ionogen, potentially, at
least. Imagine that the free base is brought into a solution
containing hydrogen ions at a concentration just sufficient to
convert one of the groups, and one only, to an ion. Perhaps the
first result will be the addition of a hydrion to one of the three
symmetrically placed dimethyl amino groups as represented by
formula IIa. Or perhaps the first result will be the stripping of
the hydroxyl group from the carbon to leave the ion IIb. Either
ion could rearrange to form the ion IIc, the first by elimination
of water and shift of electrons; the second by shift of electrons
alone. Now IIc contains the chromophore group, the quinone
group, which "accounts for" the color of the ion. It is therefore
the preferred way of representing the ion.

We may now note a matter of considerable importance. If in
fact there be a rearrangement which resembles the transformation
of IIa or IIb into IIc, the rearrangement is spontaneous and repre-
sents the persistance of the more stable form. Its *direct* control
is often beyond our power, although it may be possible by taking
advantage of the slowness of rearrangement in a rare instance to

I

IIa

$$\underset{\text{IIb}}{(CH_3)_2N-\!\!\!\!\bigcirc\!\!\!\!-\overset{\displaystyle N(CH_3)_2}{\underset{\displaystyle N(CH_3)_2}{\overset{|}{\underset{|}{C^+}}}}}$$
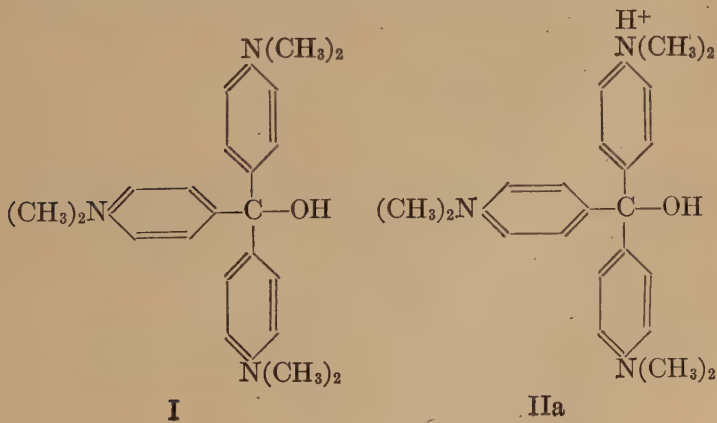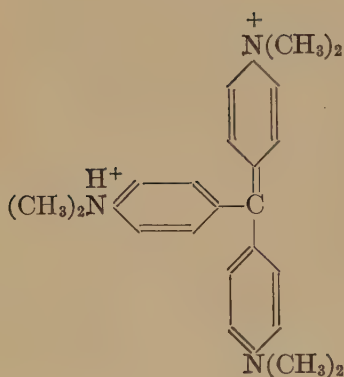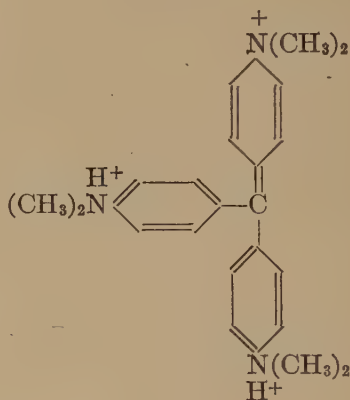
IIb

IIc

III

IV

form a derivative which rearranges less readily than the original tautomer. On the other hand the first step, whereby the ion is formed, appears to be under control by the hydrion concentration of the solution. It must not be assumed that a measurement of the "ionization constant" evaluates the primary ionization alone. The rearrangement, being spontaneous, leads to the formation of the more stable tautomer and the process of rearrangement is an integral part of the whole process of which the initial and final steps are only parts. Later we shall see that an ionization constant is a function of ionization energy. In the case at hand there may be energy involved in the rearrangement. Our measurements

are incapable of separating the two energies, and we shall find
ourselves describing the total energy change between I and IIc
as if it were that of an ionization of I directly to IIc.

Of course we must assume that any one of the forms shown is
capable of existence, in small amounts at least, under any con-
ditions. It is assumed that acetic acid molecules, for instance,
occur in minute amounts in very alkaline solutions of acetate.
Nevertheless there remains a radical distinction between the
ionogen and any one of the ions depicted above. The latter are
true tautomers, the dominance of any one of which is determined
by the stability of the internal configuration. The ionogen or a
tautomer thereof differs from the ion or a tautomer thereof by
the energy involved.

There may now be noted a rather interesting matter. By
following the elementary principles for the writing of formulas
as given for instance in *Valence* (G. N. Lewis, 1923), we arrive at
the following configuration for the group attached to the quinone
ring of IIc.

$$H + H$$
$$H:\overset{..}{C}:N:\overset{..}{C}:H$$
$$\overset{..}{H} :: \overset{..}{H}$$
$$:C:$$
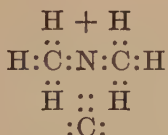
The nitrogen and each carbon are surrounded by octets of elec-
trons. However, carbon has a charge of + four to be neutralized,
nitrogen has a charge of + five to be neutralized and hydrogen a
charge of + one to be neutralized. Not only does this group
lack one electron required to fulfil these neutralizations but the
ion as a whole lacks one electron required to complete the neutral-
ization at all points. Therefore IIb and IIc differ only in the
positions of the electron pairs and of the odd electron. If one
is willing to place any significance in this rather crude way of
depicting the situation, he has already accepted some degree of
shift of an electron, if IIb and IIc are to be called tautomers in
dynamic equilibrium.

There have been attempts to relate such electron shifts, which
might be oscillations capable of resonating with radiant energy,
to color. The modern spectroscopist would doubtless not consent

to this for various reasons. Indeed the gap between the information supplied by structural chemistry and that demanded for a solution of the problem in terms of spectroscopy is so large that it would be inappropriate to our present purposes to enter the discussion and recount the many partial theoretical advances. However it would appear that a structural formula for a "tautomer" may be merely an expression of a limiting state, a state which perhaps represents crudely a main feature important to the rationalization of chemical reactions but nevertheless a state which is perhaps of no particular importance to our present purpose. We shall detect a hint of this in a further treatment of the equations.

In the meanwhile let us proceed as if the molecule or ion readjusts in large jumps to those configurations which are usually described.

Consider the case of crystal violet further. Assume that further increase in the hydrogen ion concentration will drive hydrions upon the comparatively weak, substituted amino groups forming successively the ions III and IV. Adams and Rosenstein (1914), by an analysis of the absorption bands, correlate the changes of color with the stepwise addition of hydrions to the dimethyl amino groups.

To indicate more specifically the structures *assigned to* particular systems we may deal briefly with a few of the other important indicators.

The case of phenolphthalein is often represented as follows:

V   VI   VII
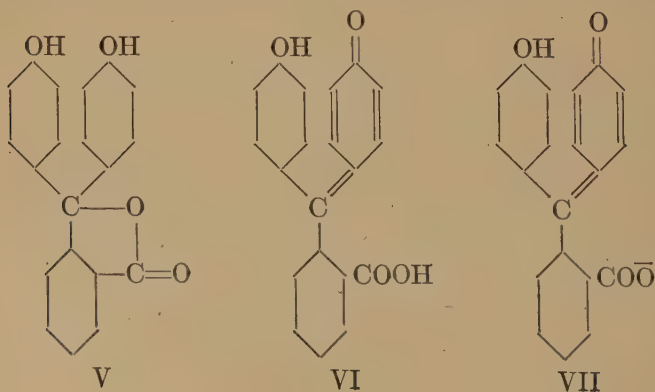
The lactone form V is a tautomer of VI which may undergo primary ionization at the carboxyl or phenolic group. The resulting ion can be represented as rearranging in several ways. A probable form is VII. This or its tautomer can then suffer secondary ionization and if the primary ion is VII the result is VIII
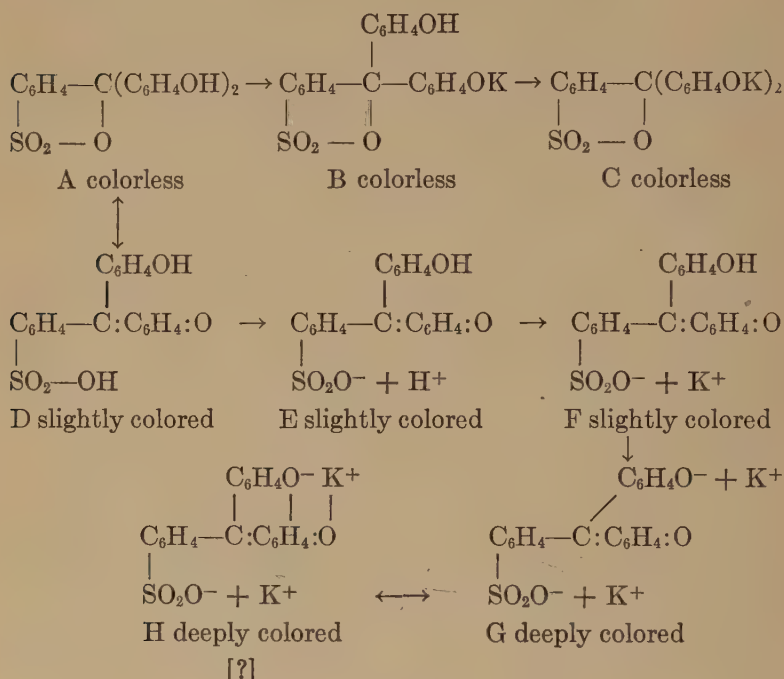

VIII   IX
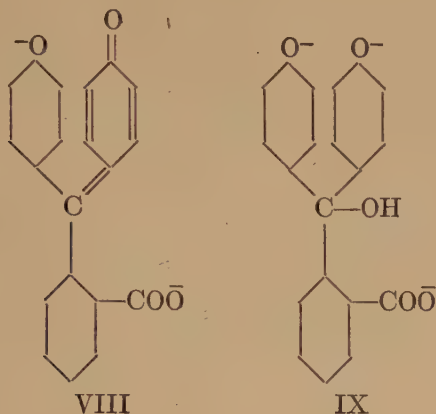
If this is rewritten with the extra electrons situated as far as possible from the center, carbon is left positive and is satisfied by addition of hydroxyl. Hence IX is sometimes used to represent the colorless carbinol found in very alkaline solutions.

According to Acree and his students (Acree, 1908) (Acree and Slagle, 1908) (Lubs and Acree, 1916) the chief color change in phenolphthalein is associated with the presence of a quinone group and with the ionization of one of the phenol groups. In the sulfon phthalein series of indicators Acree and his students (White, 1915, and White and Acree, 1918) have found much the same sort of condition.

In the sulfonphthalein group of indicators we have to deal with poly-acids; but as Acree has shown, the dissociation constant of the strong sulfonic acid group is so very much greater than that of the weak phenolic group, with which the principal color change is associated, that there is no serious interference. As shown in Chapter I we may, therefore, plot the curve for the chief "color-change" as if we were dealing with a univalent acid.

The structures of all the sulfon phthaleins are analogous to that of phenol sulfon phthalein (phenol red) whose various tautomers are given by Lubs and Acree (1916) in the following scheme:

$$C_6H_4OH$$
$$|$$
$$C_6H_4-C(C_6H_4OH)_2 \rightarrow C_6H_4-C-C_6H_4OK \rightarrow C_6H_4-C(C_6H_4OK)_2$$
$$|\quad\quad |\quad\quad\quad\quad\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |\quad\quad\quad |$$
$$SO_2 - O\quad\quad\quad\quad\quad SO_2 - O\quad\quad\quad\quad\quad\quad SO_2 - O$$

A colorless   B colorless   C colorless

$$C_6H_4OH\quad\quad\quad\quad\quad C_6H_4OH\quad\quad\quad\quad\quad C_6H_4OH$$
$$|\quad\quad\quad\quad\quad\quad\quad\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$C_6H_4-C:C_6H_4:O \rightarrow C_6H_4-C:C_6H_4:O \rightarrow C_6H_4-C:C_6H_4:O$$
$$|\quad\quad\quad\quad\quad\quad\quad\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$SO_2-OH\quad\quad\quad\quad SO_2O^- + H^+\quad\quad\quad SO_2O^- + K^+$$

D slightly colored   E slightly colored   F slightly colored

$$C_6H_4O^- K^+\quad\quad\quad\quad\quad\quad\quad\quad C_6H_4O^- + K^+$$
$$|\quad |\quad |$$
$$C_6H_4-C:C_6H_4:O\quad\quad\quad\quad C_6H_4-C:C_6H_4:O$$
$$|\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$SO_2O^- + K^+ \longleftrightarrow SO_2O^- + K^+$$

H deeply colored   G deeply colored
[?]

Of course such a table represents possibilities (some of them remote) and says nothing about the relative probability of any specific form. This must be very carefully argued by a series of analogies and by all the manifold devices of organic chemistry.

In the case of an azo indicator such as methyl orange, X, in alkaline solution,

$$SO_3^- \langle\!=\!=\!\rangle N=N \langle\!=\!=\!\rangle N(CH_3)_2 \quad\quad\quad X$$

we find the chromophore group $-N = N-$ associated with a yellow color. On driving a hydrion into this structure (by decrease of pH) there would be expected XI

$$SO_3^- \bigcirc N=N \bigcirc N(CH_3)_2 \; H^+ \qquad\qquad XI$$

which may rearrange to XII

$$SO_3^- \bigcirc \overset{H}{-}N-N= \bigcirc \overset{+}{N}(CH_3)_2 \qquad\qquad XII$$

with quinoid structure and red color. See Stieglitz (1903).

The question now is this. Given these tautomers, will their inclusion in the equilibrium equation affect the end result of the Ostwald theory?

EQUATIONS INVOLVING TAUTOMERS

In a previous section it was assumed that the theory of indicators may be treated in the simple manner outlined by Ostwald. His theory does not embrace the possibility of a radical change in structure with distinctive properties pertaining to each structure. In the section immediately preceding this, the concept of tautomerism was briefly and inadequately outlined. There we found that the ionization of one group may be followed by a rearrangement of the molecule. If the tautomer is a distinct entity there may be ascribed to any ionogenic group that it may contain a distinctive ionization constant.   Let us therefore formulate the acid-base equilibria of these systems by including the ionization constants of the separate tautomers and follow the consequences to the rather curious end.

. Merely to illustrate a principle in outline assume two tautomers HT_1 and HT_2 and let HT_1 alone ionize as an acid.   The equilibrium state for the ionization is described by

$$\frac{[T_1^-] [H^+]}{[HT_1]} = K_a \qquad\qquad (2)$$

For the equilibrium of the tautomers

$$\frac{[HT_1]}{[HT_2]} = K_T \qquad\qquad (3)$$

The combination of (2) and (3) gives:

$$\frac{[T_1^-] [H^+]}{[HT_2]} = K_a K_T = K'_a \qquad\qquad (4)$$

Now suppose that T_1^- furnishes one color and either HT_1 or HT_2 another color. Since (4) has the *form* of the ordinary equation (K_a' replacing the ordinary K_a) it is obvious that the color-change will depend on $[H^+]$ in the manner already described. Regarding the matter from another point of view we perceive that a determination of the equilibrium constant from the data for the color-change would not reveal whether this constant is a simple acid dissociation constant (K_a of 2) or a complex constant (K_a' of 4).

In one sense this situation is not unlike that which obtains in the case of an "ordinary" acid. There may be no occasion to ascribe a tautomeric form to one of these "ordinary" acids but it would require considerable skill to demonstrate that there are no tautomeric forms. There is every reason to believe that different states of hydration occur and a complete equation should contain the equilibrium constants for the hydration. We simply agree to ignore this as we agree to ignore the hydration of the hydrion in ordinary formulations. See also page 561 for a discussion of the use of the sum of the concentrations of H_2CO_3 and CO_2 in formulating carbonate equilibria.

The too simple treatment given above must now be elaborated; for the ionization of the second tautomer was neglected and may modify the conclusion. With slight changes of notation we shall follow the treatment given by Noyes (1910).

The three fundamental equations are:
Ionization of tautomer 1;

$$\frac{[T_1^-] [H^+]}{[HT_1]} = K_{a1} \tag{5}$$

Ionization of tautomer 2:

$$\frac{[T_2^-] [H^+]}{[HT_2]} = K_{a2} \tag{6}$$

Tautomerism:

$$\frac{[HT_2]}{[HT_1]} = K_T \tag{7}$$

Multiply (6) by (7), add (5) to the product and for $[HT_1]$ in the denominator of the resulting equation substitute its equivalent $\dfrac{[HT_1] + [HT_2]}{K_T + 1}$ which can be obtained from (7). There results

$$\frac{[H^+]\,([T_1^-] + [T_2^-])}{[HT_1] + [HT_2]} = \frac{K_{a1} + K_{a2}\,K_T}{1 + K_T} = K'$$

Now if $[T^-]$ represents the sum $[T_1^-] + [T_2^-]$ and if $[HT]$ represents the sum $[HT_1] + [HT_2]$, we have;

$$\frac{[T^-]\,[H^+]}{[HT]} = K' \tag{8}$$

Again we have in (8) an equation of the usual *form*. Applying to it the derivation given on page 14 we find

$$\alpha = \frac{K'}{K' + [H^+]}$$

where α is now the ratio

$$\frac{[T^-]}{[T^-] + [HT]} = \frac{[T_1^-] + [T_2^-]}{[T_1^-] + [T_2^-] + [HT_1] + [HT_2]}$$

or

$$\alpha = \frac{\text{sum of all ions}}{\text{sum of all forms}}$$

The ordinary dissociation curve will then represent the degree of color-transformation only when the sum $[T_1^-] + [T_2^-]$ is practically equal to either $[T_1^-]$ or $[T_2^-]$, according to which tautomer is associated with the color. A suggested explanation of the fact that such curves do represent closely the color degree in certain instances is that K_T is very large or very small. Formalistically, at least, an equally good suggestion is that $[T_1^-] + [T_2^-]$ or $[HT_1] + [HT_2]$ is merely an expression of a formal sum of two limiting states the shift between which is only a part, but nevertheless an integral part, of a phenomenon with which there may be associated absorption of radiant energy.

Assuming the first and more usual suggestion, we then find

that the consideration of the tautomeric equilibria only modifies the original Ostwald treatment to this extent: the found dissociation constant is a function of the several equilibrium and ionization constants involving the different tautomers. It is what Acree calls the "total affinity constant," or what Noyes calls the "apparent dissociation constant." As Stieglitz (1903) and others have pointed out, it is the state of these compounds, their existence in a dissociated or undissociated condition, which determines the stability of any one form.

But there remains a view of the together-ness of the whole set of phenomena which cannot be well formulated when we start with the assumption of independent entities having independent ionization constants. The simpler view is perhaps the better in that it permits us to conceive of the departure of the hydrion and the rearrangement as a unified process and the hydrion association and re-rearrangement as a unified process. Then the energy of ionization is linked inseparately with, or rather *is*, an integral part of any energy change involved in the rearrangement of the molecule. Because of this together-ness we appear to be dealing with a most simple case of a simple dissociation when we measure, by the means described above, the apparent ionization constant.

MULTIVALENT INDICATORS

Many indicators will not conform to the treatment of a univalent acid because there are two or more distinctive groups which may ionize either near the same level of pH or at different levels of pH.

An instance of the first is phenolphthalein. It was shown by Acree (1908) and by Wegscheider (1908) that the dissociations of the carboxyl and of a phenolic group occur near together. The proper equations to apply in such a case were developed by Acree (1907, 1908) and by Wegscheider (1908, 1915).

In the case of a sulphonphthalein the "strong" sulfonic acid group is already ionized when the phenolic group undergoes its transformation. The "spread" between the dissociation curves is then sufficient to permit the drawing of the curve of chief color change as if of a univalent acid, the undissociated portion of which is, however, the sulfonate ion.

There are also indicators with two or more basic groups, e.g.

crystal violet; and indicators of amphoteric nature, e.g. methyl orange.

In case any two ionization constants, expressed in comparable terms, have values of the same order of magnitude, it is necessary to use the complete equation and to avoid the inevitable error that would be involved in a treatment as if of a univalent acid or base.

MORE COMPLEX EQUILIBRIA

A displacement of the position of and an alteration of the form of a dissociation curve occurs when one of the components of a system precipitates. The precipitate is a special case of an aggregate which may remain in suspension. Imagine then an indicator of high molecular weight tending to form aggregates which bring its "solutions" within the category of colloidal "solutions." The presence of the aggregate *per se* interferes with simple formulation. In addition there may occur surface phenomena and various types of adsorption. These effects will be superimposed upon the basic equilibrium relations in an inseparable way and with the failure of a simple quantitative formulation the floodgates of speculation open. Many indicators such as congo red must be turned over to the students of colloid chemistry before a full account of their conduct can be given.[1] Until that account is clear these indicators and partial accounts of their conduct had best be studiously avoided except as objects of research.

THE TIME FACTOR

In the application of indicators we take advantage of the accommodating way in which they adjust their equilibria practically instantaneously and it hardly ever occurs to us to imagine the embarrassing predicament we would be in if they did not adjust instantaneously. Yet there are such indicators and one must be on his guard if the occasion arises in which they are put to use. Sørensen has one or two in his list. "China Blue" used by Bronfenbrenner (1918) is another, and a disconcerting indicator it is found to be when the very different rates of transformation of different commercial samples are compared. Equilibrium equa-

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[1] See also Zsigmondy (1924) on the degree of dispersion of some dyes which have been used as indicators.

tions are inadequate to deal with this "time effect" and equilibrium studies are easily put in jeopardy by the use of such indicators.   For discussion of the time changes we refer the reader to the very numerous papers of Hantzsch and his co-workers. Indicators involving a time adjustment are most frequently encountered among the triphenylmethane dyes.

CHAPTER VI

Approximate Determinations with Indicators

If you can measure that of which you speak, and can express it by a number, you know something of your subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory.—Lord Kelvin.

The distinctive advantages of the indicator method are the ease and the rapidity with which the approximate hydrogen ion concentration of a solution may be measured. The introduction of improved indicators, the charting of their pH ranges, better definition of degree in "acidity" or "alkalinity," and the illumination of the theory of acid-base equilibria have developed among scientific men in general an appreciation of how indefinite were those old, favorite terms—"slightly acid," "distinctly alkaline," "neutral," etc. There is now a clear recognition of the distinct difference between quantity and intensity of acidity; and for each aspect there may be given *numerical values* admitting no misunderstanding.

Furthermore the clarification of the subject has brought a perspective which may show where accuracy is unnecessary and where fair approximation is desirable. In such a case the investigator turns to the indicator method knowing that even if his results are rough they can still be expressed in numerical values having a definite meaning to others.

A very good approximation may be attained by color memory and without the aid of the standard buffer solutions or of the systems presently to be described in which the standard buffer solutions are dispensed with.

An excellent procedure for rough measurements is to utilize the colors of indicators with overlapping ranges. For instance, Cohen (1923) gives the following table.

INDICATOR	COLOR AT pH—				
	4.5	5.0	5.5	6.0	6.5
Methyl red..................	red	red	orange	yellow	yellow
Brom cresol green............	yellow	green	blue	blue	blue
Brom phenol red.............	yellow	yellow	yellow	orange	red
Brom thymol blue............	yellow	yellow	yellow	yellow	green

The reader may elaborate such a table by use of the color chart (page 65).

To establish a color memory, as well as to refresh it, a set of "permanent" standards is convenient. These may be prepared with the standard buffer solutions in the ordinary way, protected against mold growth by means of a drop of toluol, and sealed by drawing off the test tubes in a flame or by corking with the cork protected by tinfoil or paraffin. For temporary exhibition purposes long homeopathic vials make very good and uniform containers. They may be filled almost to the brim and a cork inserted, if a slit is made for the escape of excess air and liquid. The slit may then be sealed with paraffin. A hook of spring-brass snapped about the neck makes a support by which the vial may be fastened to an exhibition board. A neater container is the so-called typhoid-vaccine ampoule which is easily sealed in the flame. Standards having considerable permanency are made by sealing buffer-indicator mixtures in Pyrex glass tubes and steril-izing them by the ordinary intermittent method.

If one of a series of standards so prepared should alter, the change can generally be detected. But if all in a series should change, it may be necessary to compare the old with new stand-ards. Because such changes do occur, "permanent" standards are to be used with caution. The sulfonphthalein indicators make fairly permanent standards but methyl red which is an important member of the series of indicators recommended by Clark and Lubs (1917) often deteriorates within a short time.

As an aid to memory the dissociation curves of the indicators are helpful even when used alone. The color chart shown in Chapter III is a still better aid to memory and within the limita-tions mentioned the colors may be used as *rough* standards.

COLORIMETRIC DETERMINATION OF HYDROGEN ION CONCENTRATION
WITHOUT THE USE OF STANDARD BUFFER SOLUTIONS

We have already seen that if an indicator is an acid, its degree of dissociation, α, is related to the hydrogen ion concentration of the solution by the equation

$$[H^+] = K_a \frac{1 - \alpha}{\alpha}$$

We have also seen that if K_a, the true dissociation constant is replaced by the so-called apparent dissociation constant, K'_a, which is a function of K_a and of the constants of tautomeric equilibria, then α represents the degree of color transformation. We then have

$$[H^+] = K'_a \frac{1 - \alpha}{\alpha}$$

or the more convenient form

$$pH = pK'_a + \log \frac{\alpha}{1 - \alpha} \tag{1}$$

where α may now be considered as the degree of color transformation. If, for instance, an indicator conducts itself as a simple acid having the apparent dissociation constant 1×10^{-6} ($pK'_a = 6.0$), we can construct the dissociation curve with its central point at $pH = 6.0$. Then there can be read from the curve, or calculated from the corresponding equation, the percentage color transformation at any given value of pH. Proceeding with these simple and sometimes unjustifiable assumptions we can now devise a very simple way of measuring the degree of color transformation. The following is quoted from Gillespie (1920).

We may assume that light is absorbed independently by the two forms of the indicator, and hence that the absorption, and in consequence of this the residual color emerging, will be the same whether the two forms are present together in the same solution or whether the forms are separated for convenience in two different vessels and the light passes through one vessel after the other. Therefore, if we know what these percentages are for a given indicator in a given buffer mixture, we can imitate the color shown in the buffer mixture by dividing the indicator in the proper proportion between two vessels, and putting part of it into the acid form with excess of acid, the rest into the alkaline form with excess of alkali.

Gillespie sets up in the comparator (see page 171) two tubes, one of which contains, for example, three drops of a given indicator fully transformed into the acid form, and the other of which contains seven drops of the indicator fully transformed into the alkaline form. The drop ratio 3:7 should correspond to the ratio of the concentrations of acid and alkaline forms of ten drops of the indicator in a solution of that pH which is shown by the dissociation curve of the indicator to induce a seventy per cent transformation. If then the two comparison tubes and the tested

TABLE 14

Gillespie's table of pH values corresponding to various drop-ratios

DROP-RATIO	BROM-PHENOL BLUE	METHYL RED	BROM-CRESOL PURPLE	BROM-THYMOL BLUE	PHENOL RED	CRESOL RED	THYMOL BLUE
1:9	3.1	4.05	5.3	6.15	6.75	7.15	7.85
1.5:8.5	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2:8	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3:7	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4:6	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5:5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6:4	4.3	5.2	6.5	7.3	7 9	8.3	9.0
7:3	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8:2	4.7	5.6	6.9	7.7	8.3	8.7	9.4
8.5:1.5	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9:1	5.0	5.95	7.2	8.05	8.65	9.05	9.75
Produce acid color with	1 cc. of 0.05M HCl	1 drop of 0.05M HCl	1 drop of 0.05M HCl	1 drop of 0.05M HCl	1 drop of 0.05M HCl	1 drop of 2 per cent H_2KPO_4	1 drop of 2 per cent H_2KPO_4

solution are kept at the same volume, and the view is through equal depths of each, the two superposed comparison tubes should match the tested solution.

Barnett and Chapman (1918) applied this method with one indicator, phenol red, but without using the dissociation curve. Gillespie (1920) extended the procedure to several other indicators and made use of the dissociation curves so that he was able to smooth out to more probable values the experimental data relating drop ratios to pH. This is important because the experimental error in judging color is not inconsiderable and if the

purely empirical data be made the sole basic standardization of
the method there may be involved a systematic error, which,
added to the error of the individual measurement may make the
cumulative error unnecessarily large. That this had already
occurred was indicated by Gillespie's comparison of the values
for the drop ratios of phenol red given by Barnett and Chapman
on the one hand and the report of the bacteriologists' committee
(Conn, *et al.*, 1919) on the other hand.

Gillespie found the correspondence between the experimental
and the theoretical results predicted on the basis of the simpli-
fying assumptions mentioned above to be very good for the sul-
fonphthaleins, doubtless because of the reasons mentioned in
Chapter V. He also showed good correspondence in the case of
methyl red but reiterated the fact that phenolphthalein cannot
be treated by means of the simple dissociation curve for a mono-
acidic acid, as was mentioned in Chapter V.

In table 14 are given the pH values corresponding to various
drop ratios of seven indicators as determined by Gillespie. At
the bottom of the table are shown the quantities of acid used to
obtain the acid color in each case. Acid phosphate instead of
hydrochloric acid is used in two cases because the stronger acid
might transform the indicator into that red form which occurs
with all the sulfonphthalein indicators at very high acidities.
The 0.05 m HCl is prepared with sufficient accuracy by diluting
1 cc. concentrated hydrochloric acid (specific gravity 1.19) to
240 cc.

The alkaline form of the indicator is obtained in each case
with a drop of alkali (two drops in the case of thymol blue).
The alkali solution used for this purpose may be prepared with
sufficient accuracy by making a 0.2 per cent solution with
ordinary stick NaOH. The indicator solutions may be made up
as described on page 91. Gillespie prefers the alcoholic solution
in the case of methyl red and specifies it for soil work.

Gillespie proceeds as follows:

Test tubes 1.5 cm. external diameter and 15 cm. long are suitable for
the comparator[1] and for the strengths given for the indicator solutions.

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[1] See page 171.

It is advisable to select from a stock of tubes a sufficient number of uniform tubes by running into each 10 cc. water and retaining those which are filled nearly to the same height. A variation of 3 to 4 mm. in a height of 8 cm. is permissible. Test tubes without flanges are preferable. The tubes may be held together in pairs by means of one rubber band per pair, which is wound about the tubes in the form of two figure 8's.

It is convenient to use metal test tube racks, one for each indicator, each rack holding two rows of tubes, accommodating one tube of each pair in front and one in back. For any desired indicator a set of color standards is prepared by placing from 1 to 9 drops of the indicator solution in the 9 front tubes of the pairs and from 9 to 1 drops in the back row of tubes. A drop of alkali is then added to each of the tubes in the front row (2 drops in the case of thymol blue), sufficient to develop the full alkaline color and a quantity of acid is added to each of the tubes in the back row to develop the full acid color without causing a secondary change of color (see table 14 for quantities). . . . . The volume is at once made up in all the tubes to a constant height (within about one drop) with distilled water, the height corresponding to 5 cc.

These pairs are used in the comparator and matched with the tested solution. This tested solution is added to ten drops of the proper indicator until a volume of 5 cc. is attained and the tube is then placed in the comparator backed by a water blank.

Gillespie describes the use of the comparator (page 171) and a modification for the accommodation of sets of three tubes used when colored solutions have to be compared. He also discusses a number of minor points and cautions against the indiscriminate comparison of measurements taken at different temperatures. For the details the original papers should be consulted. Were it not that the writer has seen evidence that the method has been applied with neglect of volume or concentration relations called for by the theory involved and carefully specified by Gillespie, it would seem unnecessary to advise that the principles be understood before the method is used. Certain other misconceptions of theory and practice found in a treatment of the method by Medalia (1920) have been corrected by Gillespie (1921).

A very judicious appraisal of the value of the method was given by Gillespie in these words:

The method should be of especial use in orienting experiments, or in occasional experiments involving hydrogen ion exponent measurements, either where it is unnecessary to push to the highest degree of precision obtainable, or where the investigator may be content to carry out his

measurements to his limit of precision and to record his results in such a form that they may be more closely interpreted when a more precise study of indicators shall have been completed.

For the elaboration of certain manipulative details see Van Alstine (1920).

<div align="center">TABLE 15</div>

Table for preparation of bicolor standards with 0.016 per cent brom cresol green, 0.002 N HCl, and 0.001 N NaOH

<div align="center">Brom cresol green.   pK′ = 4.72 at 38° and 20°</div>

<div align="center">(After Hastings, Sendroy and Robson, 1925)</div>

$pH_{38°}$ and 20°	ALKALI TUBE		ACID TUBE	
	Dye	Alkali	Dye	Acid
	cc.	cc.	cc.	cc.
4.00	0.40	24.60	2.10	22.90
4.10	0.49	24.51	2.01	22.99
4.20	0.58	24.42	1.92	23.08
4.30	0.69	24.31	1.81	23.19
4.40	0.81	24.19	1.69	23.31
4.50	0.94	24.06	1.56	23.44
4.60	1.08	23.92	1.42	23.58
4.70	1.23	23.77	1.27	23.73
4.80	1.38	23.62	1.12	23.88
4.90	1.51	23.49	0.99	24.01
5.00	1.64	23.36	0.86	24.14
5.10	1.77	23.23	0.73	24.27
5.20	1.88	23.12	0.62	24.38
5.30	1.98	23.02	0.52	24.48
5.40	2.07	22.93	0.43	24.57
5.50	2.14	22.86	0.36	24.64
5.60	2.21	22.79	0.29	24.71
5.70	2.26	22.74	0.24	24.76
5.80	2.31	22.69	0.19	24.81

Hastings, Sendroy and Robson (1925) have systematized the Gillespie method as follows. The indicator solution specified in each of the following tables (15 to 18) are added to each tube from a micro burette. Then either 0.001 N HCl, 0.01 N or 0.001 N NaOH solution is added to bring the volume to 25 cc. "The tubes are stoppered or sealed and kept in a dark cupboard. When sealed, the solutions are stable for several months."

The stock indicator solution (0.1 per cent) are prepared by the procedure noted on page 91. These are diluted as follows.

	FINAL CONCENTRATION	STOCK SOLUTION DILUTED TO 200 cc.
	per cent	cc.
Phenol red......................................	0.0075	15
Brom cresol purple.............................	0.008	16
Chlor phenol red...............................	0.010	20
Brom cresol green..............................	0.016	32

TABLE 16

Table for preparation of bicolor standards with 0.01 per cent chlor phenol red, 0.001 N HCl, and 0.01 N NaOH

Chlor phenol red.   pK' = 5.93 at 38°, and 6.02 at 20°

(After Hastings, Sendroy and Robson, 1925)

pH$_{38°}$	ALKALI TUBE		ACID TUBE		pH$_{20°}$
	Dye	Alkali	Dye	Acid	
	cc.	cc.	cc.	cc.	
5.00	0.26	24.74	2.24	22.76	5.09
5.10	0.32	24.68	2.18	22.82	5.19
5.20	0.39	24.61	2.11	22.89	5.29
5.30	0.48	24.52	2.02	22.98	5.39
5.40	0.57	24.43	1.93	23.07	5.49
5.50	0.68	24.32	1.82	23.18	5.59
5.60	0.80	24.20	1.70	23.30	5.69
5.70	0.93	24.07	1.57	23.43	5.79
5.80	1.07	23.93	1.43	23.57	5.89
5.90	1.20	23.80	1.30	23.70	5.99
6.00	1.35	23.65	1.15	23.85	6.09
6.10	1.50	23.50	1.00	24.00	6.19
6.20	1.63	23.37	0.87	24.13	6.29
6.30	1.75	23.25	0.75	24.25	6.39

USE OF "ONE-COLOR" INDICATORS

If an indicator has only one color, for instance if it is yellow in the alkaline form and colorless in the acid form, it is evident that the method employed by Gillespie may be used with the elimination of one of the sets of tubes. Thus if 10 cc. of a tested solution containing 1 cc. of para nitrophenol matches 10 cc. of

an alkaline solution containing 0.2 cc. of the same solution of the same indicator, it is known that the tested solution has induced a 20 per cent transformation of the indicator. Then α is 0.2. If now K'_a has been determined, and if it has been shown that the simple dissociation formula holds for the indicator in use, the following equation may be solved for pH.

$$pH = pK'_a + \log \frac{\alpha}{1 - \alpha}$$

TABLE 17

Table for preparation of bicolor standards with 0.008 per cent brom cresol purple, 0.002 n HCl, and 0.01 n NaOH

Brom cresol purple.   pK' = 6.09 at 38°, and 6.19 at 20°
(After Hastings, Sendroy and Robson, 1925)

pH$_{38°}$	ALKALI TUBE		ACID TUBE		pH$_{20°}$
	Dye	Alkali	Dye	Acid	
	cc.	cc.	cc.	cc.	
5.60	0.61	24.39	1.89	23.11	5.70
5.70	0.72	24.28	1.78	23.22	5.80
5.80	0.85	24.15	1.65	23.35	5.90
5.90	0.99	24.01	1.51	23.49	6.00
6.00	1.12	23.88	1.38	23.62	6.10
6.10	1.26	23.74	1.24	23.76	6.20
6.20	1.40	23.60	1.10	23.90	6.30
6.30	1.55	23.45	0.95	24.05	6.40
6.40	1.68	23.32	0.82	24.18	6.50
6.50	1.80	23.20	0.70	24.30	6.60
6.60	1.91	23.09	0.59	24.41	6.70
6.70	2.01	22.99	0.49	24.51	6.80
6.80	2.09	22.91	0.41	24.59	6.90
6.90	2.16	22.84	0.34	24.66	7.00

This procedure has been developed by Michaelis and coworkers; *Biochem. Z.* (1920) **109**, 165; *Biochem. Z.* (1921) **119**, 307; *Deut. med. Wochenschr.* (1920) **46**, 1238; **47**, 465, 673; *Z. Nahr. Genussm.* (1921) **42**, 75; *Z. Immunitätsf.* (1921) **32**, 194; *Wochenschrift Brau.* (1921) **38**, 107.

The following revisions of their tables are taken from the 1926 edition of *Praktikum der Physikalischen Chemie* by Michaelis.

In the cases of phenolphthalein and Alizarine Yellow GG the

TABLE 18

*Table for preparation of bicolor standards with 0.0075 per cent phenol red,
0.001 n HCl, and 0.01 n NaOH*

Phenol red.   pK′ = 7.65 at 38°, and 7.78 at 20°

(After Hastings, Sendroy and Robson, 1925)

pH$_{38°}$	ALKALI TUBE		ACID TUBE		pH$_{20°}$
	Dye	Alkali	Dye	Acid	
	cc.	cc.	cc.	cc.	
6.70	0.25	24.75	2.25	22.75	6.83
6.80	0.31	24.69	2.19	22.81	6.93
6.90	0.38	24.62	2.12	22.88	7.03
7.00	0.46	24.54	2.04	22.96	7.13
7.10	0.55	24.45	1.95	23.05	7.23
7.20	0.65	24.35	1.85	23.15	7.33
7.30	0.77	24.23	1.73	23.27	7.43
7.40	0.90	24.10	1.60	23.40	7.53
7.50	1.04	23.96	1.46	23.54	7.63
7.60	1.18	23.82	1.32	23.68	7.73
7.70	1.32	23.68	1.18	23.82	7.83
7.80	1.46	23.54	1.04	23.96	7.93
7.90	1.60	23.40	0.90	24.10	8.03
8.00	1.73	23.27	0.77	24.23	8.13
8.10	1.85	23.15	0.65	24.35	8.23
8.20	1.95	23.05	0.55	24.45	8.33

TABLE 19

"One-color" indicators

COMMON NAME	CHEMICAL NAME	COLOR	pK AT 18°	RANGE	SOLUTION
β-dinitrophenol.....	1-oxy-2,6-dinitroben-zene	yellow	3.69	2.2– 4.0	0.1 gram in 300 cc. water
α-dinitrophenol.....	1-oxy-2,3-dinitroben-zene	yellow	4.06	2.8– 4.5	0.1 gram in 200 cc. water
γ-dinitrophenol.....	1-oxy-2,5-dinitroben-zene	yellow	5.15	4.0– 5.5	0.1 gram in 200 cc. water
p-nitrophenol.......	1-oxy-4-nitrobenzene	yellow	7.18	5.2– 7.0	0.1 gram in 100 cc. water
m-nitrophenol......	1-oxy-3-nitrobenzene	yellow	8.33	6.7– 8.4	0.3 gram in 100 cc. water
Phenol phthalein...	phenol phthalein	red	(9.73)	8.4–10.5	0.04 gram in 30 cc. al-cohol + 70 cc. water
Alizarin yellow GG (salicyl yellow)...	m-nitrobenzene-azo-salicylic acid	yellow	(11.16)	10.0–12.0	0.05 gram in 50 cc. al-cohol + 30 cc. water

TABLE 20

pK values of "one-color" indicators at different temperatures

TEMPERATURE	β-DINITRO-PHENOL (1:2:6)	α-DINITRO-PHENOL (1:2:4)	γ-DINITRO-PHENOL (1:2:5)	p-NITRO-PHENOL 1:4	m-NITRO-PHENOL 1:3
°C.					
0	3.70	4.16	5.24	7.39	8.47
5	3.76	4.13	5.21	7.33	8.43
10	3.74	4.11	5.18	7.27	8.39
15	3.71	4.08	5.16	7.22	8.35
18	3.69	4.06	5.15	7.18	8.33
20	3.68	4.05	5.14	7.16	8.31
25	3.65	4.02	5.11	7.10	8.27
30	3.62	3.99	5.09	7.04	8.22
35	3.59	3.96	5.07	6.98	8.18
40	3.56	3.93	5.04	6.93	8.15
45	3.54	3.91	5.02	6.87	8.11
50	3.51	3.88	4.99	6.81	8.07

TABLE 21

Relation of apparent degree of color, α, to pH

Phenolphthalein

α	pH	α	pH	α	pH
0.01	8.45	0.16	9.10	0.55	9.80
0.014	8.50	0.21	9.20	0.60	9.90
0.030	8.60	0.27	9.30	0.65	10.00
0.047	8.70	0.34	9.40	0.70	10.1
0.069	8.80	0.40	9.50	0.75	10.2
0.090	8.90	0.45	9.60	0.80	10.3
0.120	9.00	0.50	9.70		

TABLE 22

Relation of apparent degree of color, α, to pH

Alizarin yellow GG

α	pH	α	pH
0.13	10.00	0.56	11.20
0.16	10.20	0.66	11.40
0.22	10.40	0.75	11.60
0.29	10.60	0.83	11.80
0.36	10.80	0.88	12.00
0.46	11.00		

color-change does not follow the type α-curve for a univalent acid. Tables 21 and 22 give the empirical values for α for use with the ideal equation.

Calculations are aided by the use of a table relating α to $\log \dfrac{\alpha}{1 - \alpha}$. Such a table, somewhat more elaborate than that required for this special purpose, will be found on page 677 of the Appendix.

TABLE 23

Composition of color standard

m-nitrophenol

Tube number	1	2	3	4	5	6	7	8	9
Cubic centimeters of indicator	5.2	4.2	3.0	2.3	1.5	1.0	0.66	0.43	0.27
pH	8.4	8.2	8.0	7.8	7.6	7.4	7.2	7.0	6.8

p-nitrophenol

Tube number	10	11	12	13	14	15	16	17	18
Cubic centimeters of indicator	4.05	3.0	2.0	1.4	0.94	0.63	0.4	0.25	0.16
pH	7.0	6.8	6.6	6.4	6.2	6.0	5.8	5.6	5.4

2,5-dinitrophenol (γ dinitrophenol)

Tube number	19	20	21	22	23	24	25	26
Cubic centimeters of indicator	6.6	5.5	4.5	3.4	2.4	1.65	1.1	0.74
pH	5.4	5.2	5.0	4.8	4.6	4.4	4.2	4.0

2,4-dinitrophenol (α dinitrophenol)

Tube number	27	28	29	30	31	32	33	34	35
Cubic centimeters of indicator	6.7	5.7	4.6	3.4	2.5	1.74	1.20	0.78	0.51
pH	4.4	4.2	4.0	3.8	3.6	3.4	3.2	3.0	2.8

With these data we are now prepared to measure pH values without the use of standard buffer solutions.

Test tubes must be of equal bore. A measured amount of the solution to be tested (e.g. 10 cc.) is mixed with the proper indicator in such amount that a rather weak color is developed. To a second test tube containing 9 cc. 0.1 M Na_2CO_3 (for nitrophenols only) there is added such a volume of the indicator solution that the color developed approximately matches that of the first tube. The volume of the second tube is now made up to the volume of the first. If the two tubes do not match in color, another trial

is made with more or less indicator until a color match is obtained. The amount of fully transformed indicator in the second tube then corresponds to that amount of indicator in the first tube which has been transformed to the colored tautomer. Let us assume that 1.0 cc. was added to the tested solution and that a color match occurs when 0.1 cc. of the same indicator solution was placed in the second alkaline tube and made up to the volume of the first. Then the percentage color transformation induced by the tested solution was 10.

Hence $\alpha = 0.1$ and $\log \dfrac{\alpha}{1 - \alpha} = -0.95$.

If the indicator used was p-nitrophenol and the temperature was 20°C. pH $= 7.16 - 0.95 = 6.21$ (6.2).

For *routine* work in the range pH 2.8 to 8.4 Michaelis (1921) recommends the following system. See table 23.

To uniform test tubes are added *seriatim* the volumes of indicator solution given in table 23, the indicator solution being prepared by diluting the stock solutions (page 128) ten times with 0.1 M Na_2CO_3 solution. Each tube is now filled to a 7 cc. mark with the soda solution. (In the original paper Michaelis and Gyemant describe dilutions with N/100 NaOH solution.)

The test tubes are sealed and when not in use are protected from the light.

To test a solution for its pH value, 6 cc. are taken and 1 cc. indicator solution added. The solution is then compared with the standards in a comparator, see page 171, figure 29.

Empirically, Michaelis finds that if there be placed over the comparator holes a ground glass and a glass of cobalt blue, the color *quality* of two tubes will be very different when there is no match. This increases the differentiating ability of the eye and makes the use of the nitrophenols with colored solutions, such as urine, much more satisfactory. The glass of cobalt blue should be selected by trial for a satisfactory density.

For finding the pH values of waters Michaelis (1921) operates as follows:

A stock solution containing 0.3 gram pure m-nitrophenol in 300 cc. distilled water is diluted before use by adding to 1 cc. of the stock 9 cc. distilled water. There are used flat bottom

tubes of about 25 cm. height and 14 mm. internal diameter having such uniformity that 40 cc. of water will stand at a height of between 22 and 23 cm. To six such tubes are added *seriatim* 0.25; 0.29; 0.33; 0.38; 0.45 and 0.50 cc. of the diluted m-nitrophenol solution. To each tube are added 40 cc. of an approximately N/50 NaOH solution freshly prepared by dilution of an approximately normal solution. These are the standards.

To test a water, 40 cc. are added to a tube of correct dimensions and to this is added sufficient indicator to develop a color within the range of the standards, preferably near the brighter of the standards. Comparison is now made as in Nesslerization, after having waited two minutes for completion of the mixing.

TABLE 24

Effect of salt on pK of m-nitrophenol

MOLECULAR SALT CONTENT	$\log \dfrac{1}{K'_a}$
0–0.01	8.33
0.05	8.28
0.10	8.23
0.15	8.22
0.20	8.18
0.3–0.6	8.17
to 1.0	8.15

The amount of indicator in the alkaline, matching standard corresponds to the amount transformed to the colored form by the tested solution. Therefore, the cubic centimeters of indicator in the standard divided by the cubic centimeters in the tested solution is α, the degree of color transformation, or when multiplied by 100, the percentage color transformation.

Michaelis and his co-workers have tabulated corrections for temperature and for salt concentrations. The operator should determine for himself not only the order of accuracy required in his problem but his own ability to make readings with that precision which will make corrections significant. He may then refer to the original papers for tables giving corrections for salt effects and for temperature. The order of magnitude of these corrections may be seen in tables 20 and 24.

For m-nitrophenol Michaelis and Krüger give the values of

$\log \dfrac{1}{K'_a}$ at 17°C. in solutions of the indicated salt concentrations shown in table 24.

In spite of the fact that the nitro-compounds used by Michaelis and Gyemant are of wan color and those tried in the survey made by Clark and Lubs were neglected for this reason, Michaelis and Gyemant describe the application of their method to colored solutions. In this use the colored glass is essential.

Advantage is taken of the fact that many solutions are inappreciably altered in pH by diluting five or even ten times (see page 40). For dilution, Michaelis and Gyemant use freshly boiled NaCl solution of a concentration approximately that of the test solution. If on dilution the natural color still interferes with the use of an indicator, the natural color may be duplicated in the standard by the use of supplementary dyes such as Sørensen uses. Or, *if addition of alkali does not alter the natural color of the solution under test*, the standard may be made up with an alkaline solution of the tested solution itself. In this case it is necessary to be on guard against the buffer action and to add alkali until no increase in the color of the indicator is observed.

Without doubt the preferable procedure to follow when applying the Michaelis and Gyemant method or any other method to colored solutions is to use the "comparator" described on page 172 and illustrated in figure 29, page 171. The blue glass (see page 131) is held before the holes by a pair of clips.

The method of Michaelis and Gyemant is fundamentally the same as that of Gillespie and should, therefore, be used with the qualifications which Gillespie has stated. There is a distinct advantage in the use of the nitrophenols for they have been found to have relatively small "protein" and salt effects, and do not show the errors with alkaloids that appear with the use of sulfonphthaleins. It is sometimes necessary to use very high concentrations of the indicator, and in such circumstances one must be on guard against the effect of the indicator itself or of impurities. Only the purest grades of nitrophenols should be used. Impure samples are almost useless.

Inasmuch as the method inherently is capable of high accuracy it may be asked why its description is relegated to a chapter entitled "approximate determinations." If the reader will reflect

he will remember that any numerical value reached by the application of this method depends upon the value of the dissociation constant. There remain larger discrepancies in the values for some of the indicators than are warranted by the accuracy of available methods if applied to the same solutions. But, as we shall see, a dissociation constant formulated by the classical methods, is subject to some change in value as the nature of the solution (e.g., salt content) changes. It is therefore preferable to recast the equations into terms of activities (see Chapter XI) and when this is done the true dissociation constant may have a very different numerical value than has the apparent constant at a given salt content of the solution. As this edition goes to press the period is just beginning when the characteristic constants of indicators are being redetermined both with the aid of spectrophotometric accuracy and with the aid of modern reformulation. Pending the outcome we must regard the application of the method in question, when performed with the data available, as having been *standardized by reference to* the standard buffer method and with all the systematic errors attendant upon a secondary standardization.

Indicator papers. Although a favorite form of indicator is the deposit on a strip of paper (for example the familiar litmus paper) it is to be avoided unless the use of an indicator solution is precluded. It is to be avoided because the factors involved in the reaction between solutions and indicator are made complex by the capillary action of the paper or the material entrained in these capillaries. On the other hand there are occasions when an approximate measure of pH is sufficient and when an indicator-paper is to be preferred. On such occasions it is desirable to know the difficulties to be encountered.

We are indebted to Walpole (1913) and others and particularly to Kolthoff (1919, 1921) for investigations on this subject. Kolthoff has given particular attention to the sensitivity of indicator papers when used in titrations, a situation where there is generally but little buffer action near the end-point. Under such circumstances there are to be regarded a number of details which are described at length in Kolthoff's papers. Several of these details will be perceived if we describe some of the more important aspects of the indicator-paper method of determining pH.

In general one must ride either horn of the following dilemma. The paper is sized, in which case the buffer action of the tested solution must be strong enough and allowed time enough to overcome the buffer action of the sizing. Or the paper has the qualities of filter paper, in which case the solution tested will spread and leave rings of different composition formed by the adsorptive power of the capillaries.

Kolthoff found that various treatments and selections of filter paper are of secondary importance, so the choice lies between sized and unsized paper. Certain coloring matters are adsorbed by filter paper so that a separation is possible and the clear solution can be found in a ring about the point of contact between a tested colored solution and the indicator paper. But beyond this ring is a much more dilute one and unless one knows the properties of the system under examination it is not easy to estimate correctly the pH of the solution from the appearance of the paper.

In any case the paper should be left in contact with the tested solution a generous length of time, for the establishment of equilibrium may be very slow (Walpole), and there must be instinctively exercised a mental plotting of the time curve.

If, after having exhausted all other methods, it is found that the indicator-paper method is the better adapted to a particular set of circumstances, the procedure should be calibrated to the purpose at hand rather than forced to render accurate pH values.

Rebello (1922) replaces paper by cotton thread which he draws through the tissue he examines. Wulff (1926) uses transparent membranes of cellulose derivatives.

See Kolthoff and Furman's book *Indicators* for further discussion of indicator papers.

Dilution. As indicated in Chapter II a well buffered solution may often be moderately diluted without seriously altering the pH.

When dealing with complex solutions which are mixtures of very weakly dissociated acids and bases in the presence of the salts, and especially when the solution is already near neutrality, dilution has a very small effect on pH, so that if we are using the crude colorimetric method of determining pH, a five-fold dilution of the solution to be tested will not affect the result through the small change in the actual hydrogen ion concentration. Differences which may be observed are quite likely to be due to change in the protein or salt content.

For accurate work with dilutions there should be involved the principles discussed in Chapter XXV.

The salt content of the standards undoubtedly influences the indicators and should be made as comparable as is convenient with the salt content of the solutions tested when these are diluted to obtain a better view of the indicator color.

In the examination of soil extracts colorimetrically little could be done were the "soil-solution" not diluted. Whatever may be the effect it is certain that the correlations between the pH values of such extracts and soil conditions is proving of great value (see Chapter XXX). Wherry has developed a field kit of the sulfonphthalein indicators with which he has found some remarkable correlations between plant distribution and the pH of the native soils. This field kit is now on the market.

A good example of the application of the dilution method is given in a paper by Sharp and McInerney (1926). They dilute milk, whey and cream with as much as nineteen volumes of water in order to lower the turbidity adequately. They then apply their statistical study of corrections to be made to bring the colorimetric readings into conformity with the hydrogen electrode measurements of the undiluted solution. They tabulate these corrections for convenience in routine examinations.

The use of indicators in bacteriology. Perhaps no other science requires such continuous routine use of indicators as does bacteriology. This use is chiefly in the adjustment of the reaction of culture media and in the testing of the direction and limits of fermentation. While these are but examples, the frequency with which they become matters of routine warrants a brief outline of special procedures.

If experience has shown that the pH of the medium may lie within a zone about 0.5 unit of pH wide, it is sufficient to add unstandardized acid or alkali, as the case may be, until a portion of the medium tested with the proper indicator in proper concentration approximately matches that color standard shown in the color chart of page 65 corresponding to the pH value to be approximated. This requires experience in overcoming the confusing effect of the natural color of the medium and also a well established sense of color memory. The beginner should proceed in some such way as the following.

It is desired, for instance, to adjust a colorless medium to pH 7.5. The medium as prepared is somewhat below the final volume. A quick, rough test at room temperature shows that the pH value lies between 6.0 and 6.5. Therefore, alkali must be added. The alkali solution to be used need not be standardized but may be about 1 normal. An exact one-in-ten dilution of this is run into 5 cc. of the medium to which have been added 5 drops of phenol red solution. Titration is continued until the color nearly matches 10 cc. of standard buffer "7.5." The tube of medium is now diluted to 10 cc. so that a color comparison may be made between test solution and standard, each containing the same concentration of indicator. The tubes are viewed through equal depths of solution. If the desired point, 7.5, has been overstepped, another trial is made. If 7.5 is not reached a moderate addition of alkali may be made without serious violation of volume requirements, and a second reading is taken.

After making estimates of the pH values in the two readings an interpolation is made of the amount of dilute alkali required to bring the medium to exactly pH 7.5. From this is calculated the amount of the stronger alkali required for the main portion. After adding this, a check determination is made. When finally adjusted the medium is diluted to its final volume Most culture media suffer alterations of their pH values during sterilization and consequently allowance for this must be made if the final pH value is to be exact. This allowance will vary with the medium but can easily be determined for a standard medium prepared under uniform conditions.

When the color or turbidity of a tested solution interferes with direct color comparisons proceed as above but make comparisons by means of the Walpole compensation method described on page 171.

It need hardly be said that if the requirements of an organism are such that the desired pH value cannot be obtained with phenol red a more suitable indicator is selected from table 11 and if the medium requires the addition of acid an unstandardized acid solution approximately normal (or stronger) and an exact 1:10 dilution of this are substituted for the alkali solutions mentioned above.

In testing fermentations it often happens that the final hydro-

gen ion concentration is of more significance than the amount of acid or alkali formed; but the two distinct types of data are not to be confused to the complete displacement of either.

It is sometimes convenient to incorporate the indicator with the medium, provided the indicator is not reduced or destroyed by the bacterial action. The sulfonphthaleins are particularly useful for they are not reduced except by the more active anaerobes. Brom cresol purple replaces litmus in the common milk-fermentation tests without introducing that confusion which the reduction of litmus causes. It reveals differences in pH even beyond the range of its usefulness for ordinary measurements, passing from a greyish blue in normal milk to more and more brilliant yellows with the development of acidity, and to a deep blue with the development of alkalinity. For further details see Clark and Lubs (1917).

In the method of Clark and Lubs (1915, 1916) for the differentiation of the two main groups of the coli-aerogenes bacteria, as well as in the similar method of Avery and Cullen (1919) for separating streptococci, the composition of the medium is so adjusted to the metabolic powers of the organisms, that the reaction is left acid to methyl red in one case, and alkaline in the other. No exact pH measurements are necessary. In cases where large numbers of cultures falling within the range of one indicator are to be tested, the cultures may be treated with the indicator and compared by grouping. A careful determination made upon one member of a homogeneous group will serve for all. In this way large numbers of cultures may be tested in a day.

Special uses. While on the subject of approximate determinations with indicators a word may be said about the usefulness of the quick, rough test.

Almost every investigator has come to realize that among the mistakes in labeling chemicals the more frequent are cases in which a basic salt is labeled as an acid salt and *vice versa*. A solution of Na_2HPO_4, for example, has a pH value, which, while easily displaced (see fig. 4), distinguishes it definitely from a solution of NaH_2PO_4 or Na_3PO_4. Indeed some idea may be obtained of the degree of impurity if the pH value of a dilute solution is displaced definitely from about pH 8.5. Some serious accidents have occurred in medical practice by the use of solutions purported

to be neutral and too late found to be acidic. One short, swift test with an indicator could have· revealed the situation, and averted the accident.

Indeed there are a great many substances solutions of which have either a buffered and definite pH value, as in the case of acid potassium phthalate, or else a pH value easily displaced by impurities from that of the absolutely pure substance but still falling within limits, as in the case of the primary and secondary phosphates. When properly defined, such values can be made part of the specifications for purity. Especially in the case of drugs which are often used beyond the reach of the assay laboratory a simple indicator test should prove helpful as suggested by Evers (1921) and especially emphasized by Kolthoff (1921).

MICRO COLORIMETRIC METHODS

The majority of micro-methods[2] follow the main principles hitherto described but with greater or lesser reduction in the dimensions of the vessels. Such are the capillary tubes employed by Walther and Ulrich (1926), Needham and Rapkine. Rapkine's capillary tubes, used for comparison with a single cell which has been injected with an indicator, are made of varying diameter in order that there may be selected a portion of the capillary of the same diameter as the cell.[3] Vlès (1926) describes a micro colorimeter for use on the microscope stage.

Spotting. When only small quantities of solution are available or when highly colored solutions are to be roughly measured, their examination in drops against a brilliant white background of "opal" glass is often helpful. In the examination of colorless solutions comparisons with standards may be made as follows. A drop of the solution under examination is mixed with a drop of the proper indicator solution upon a piece of opal glass. About this are placed drops of standard solutions and with each is mixed a drop of the indicator solution used with the solution under examination. Direct comparison is then made. Felton, who developed details in this method for the examination of small quantities of solutions used in tissue-culture investigations, found

[2] See also Pfeiffer (1927), Vlès (1926) and Lindhard (1921) on micro-colorimetric methods. Cf. Ellis (1925).

[3] Personal communication.

mixtures of indicators of particular value for orientation. (See page 96.) Mixtures are used only as "feelers." The opal glass or porcelain upon which the tests are to be made should be carefully tested for the absence of material seriously affecting the acid-base equilibria of the material under examination. Errors due to unequal drops, evaporation and impurity of indicator are to be watched for. For further details see Felton (1921).

To what extent the mixture of as much as 50 per cent by volume of indicator solution and tested solution causes an error can only be judged in the specific case.

From the spot-plate with flat surface and drops of any size that can be made, we come to the spot-plate with depressions to hold larger quantities; and then to small glass cells such as Brown (1923) employs and such as the LaMotte Co. uses in one of their commercial sets.

PRECIPITATING INDICATORS

Naegeli (1926) employs the principle, briefly noted on page 583, that precipitations may occur within narrow ranges of pH. He therefore selects organic acids the undissociated forms of which are very little soluble.

The variation of the precipitation point with the buffer suggests a restudy in terms of activities. See page 583.

CHAPTER VII

The Application of Spectrophotometry, Colorimetry, Etc.

How that element washes the universe with its enchanting waves!
. . . . 'Tis the last stroke of Nature; beyond color she cannot go.
—Emerson.

INTRODUCTION

The marvelous color-change of an indicator invites scrutiny of
the internal structure. Why should the mere act of ionization
initiate a radical change in the response to radiation? Theory
relating structure to absorption of radiant energy has not yet
attained the certitude that will doubtless arrive in time. There-
fore, we had best resist the temptation to look into this tantalizing
subject lest our attention be diverted from the present task,
which is to formulate the fact of absorption of radiant energy in
a manner which will contribute to exactitude in measurement of
pH-values.

ABSORPTION

As radiant energy of any wave-length advances through a
material medium it suffers some absorption. Visible radiant
energy is absorbed but little by water and by optical grades of
glass; but in refined measurements absorption by these relatively
"transparent" materials must be taken into account. Usually
absorption by solutions is somewhat selective. Absorption is
both selective and effective in solution of those "dyes" which are
used as indicators. Thus, if an alkaline solution of cresol red is
viewed through a spectroscope, there appears in the spectrum a
dark band, the position of which indicates that the stimuli of the
colors yellow and green have been very effectively obstructed.
So far as *relative absorption* of the radiant energy is concerned,
this is shown quantitatively by the curves of figure 20 where the
ordinate is a measure of relative absorption and the abscissa
is divided in such a way as to show approximately the relative
positions of lines of various wave-length as distributed in the

141

spectrum of a prism instrument. From this curve it is evident that, in addition to relatively great absorption centered at the wave-length (λ)[1] of $m\mu = 572$, there is appreciable absorption by
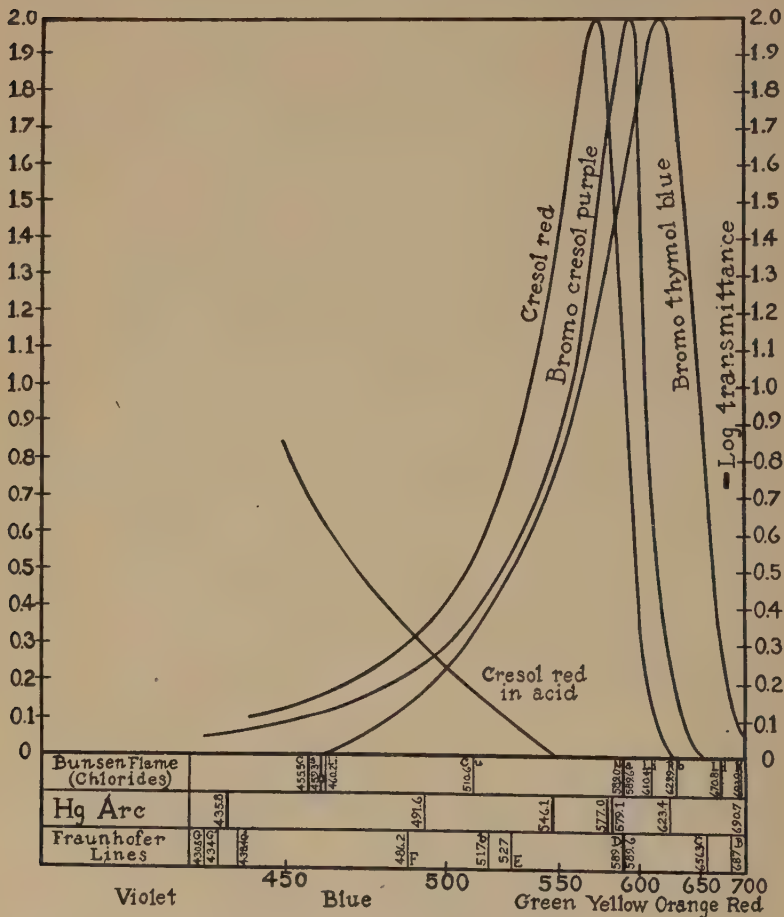
FIG. 20. ABSORPTION CURVES OF INDICATORS

cresol red within the range $m\mu$ 450 to $m\mu$ 610. Quantitative measurement of absorption and the charting of the absorption

[1] $\lambda \equiv$ general symbol for wave-length. $m\mu \equiv$ milli micron $\equiv$ meters $\times 10^{-9}$. One $m\mu = 10$ Ångstrom units.

band provides data for identification of an indicator and for tests of purity. A special application of the data to the determination of pH values will presently be outlined.

Neglect for the moment absorption by the solvent and by the glass walls of the container. Consider the absorption which occurs when radiant energy of *one definite wave-length*, λ, passes through a homogeneous solution of some absorbing substance contained in a cell the end-plates of which are plane-parallel, the propagation through the cell and solution being rectilinear.

In advancing through an infinitesimal length, dl, of the solution, the radiant energy of the given wave-length suffers the loss of some certain fraction of its power,[2] P. Within the next infinitesimal length the remaining power is reduced by the same fraction. Accordingly, the decrease of power per element of length is proportional to the power of the radiant energy in this length.

$$\frac{-\,d\mathrm{P}}{dl} = \mathrm{k}'\mathrm{P} \tag{1}$$

Now let the power incident at the first surface of the solution be P_1 and that emergent at the second surface be P_2. When these limits are used in the integration of equation (1) there is obtained equation (2)

$$-\,ln\,\frac{\mathrm{P}_2}{\mathrm{P}_1} = \mathrm{k}'l \tag{2}$$

In this equation *ln* (*logarithmus naturalis*) symbolizes (natural) logarithms to the base e.

The decline of radiant power within any infinitesimal length of the solution should be proportional to the number of absorbing molecules encountered. This number may be considered proportional to the concentration, c, of the dye under a given set of conditions. Therefore, (1) becomes (3). Integration of (3) between the limits P_1 and P_2 yields (4)

$$\frac{-\,d\mathrm{P}}{dl} = \mathrm{kcP} \tag{3}$$

[2] Since ratios of powers are to be used, intensity might be substituted here for power.

$$- ln \frac{P_2}{P_1} = kcl \tag{4}$$

The ratio $\frac{P_2}{P_1}$ is that fraction of the power of the incident radiant energy which emerges.   This ratio is called the *transmittance* and is symbolized by T.   Introducing T and changing the constants of (2) and (4) to correspond with the conversion of natural logarithms to common logarithms we have from (2) and from (4) equations (5) and (6) respectively.

$$-\log T_\lambda = lK'_\lambda \quad \text{(Lambert's Law)} \tag{5}$$
$$-\log T_\lambda = lcK_\lambda \quad \text{(Beer's Law)} \tag{6}$$

The subscript λ is used to emphasize the fact that specific values for the indicated terms depend upon the wave-length (λ) of the radiant energy.

Here it may be noted that any relation between the transmittance at a given wave-length and the wave-length is determined by the specific properties of the absorbing system.   In other words the position and shape of the absorption curve is characteristic of a given system.   With the cause of this, or with the empirical formulation of a relation between T_λ and λ as λ varies, we are not now concerned.   We are concerned only with the acceptance of the fact as a specificity to put to our present uses.   For a brief discussion of variation of T_λ with variation of λ see Thiel and Diehl (1927) page 517 ff. but especially the Report of the Committee on Spectra and Constitution, 1926, British Association.

Equation (5) is an expression of Lambert's law of absorption and is believed to be universally applicable.   Equation (6), which involves concentration of the absorbing species, must be used with caution; for, although there will presently be noted cases in which apparent deviation from this so-called Beer's law is readily explained and indeed put to use, there are cases in which observed deviations have not been explained.

When the length, l, and the concentration, c, are each unity

$$- \log T = K$$

K is called the specific transmissive index.   Its value as determined by a measurement of T *at a given wave-length* will of course depend upon the unit adopted for l and c.   The unit of length is usually the centimeter; but the

unit of concentration is frequently changed to the convenience of special problems. Were c the concentration of *total* dye, as it is in the usual statement of Beer's law, and were one mole per liter the unit of concentration, K would be the *molar transmissive index*. The term *absorption index* arises from the fact that the magnitude of K is a measure of the extent of the relative absorption. If $\frac{P_2}{P_1}$ is T, the transmittance, $1 - \frac{P_2}{P_1}$ may be called the absorptance A, a term little used.

The term "*extinction coefficient*" arises in the following way. Were *all* the radiant power incident at the first surface to be absorbed (extinguished) when the radiation reached the second surface, $\frac{P_2}{P_1}$ would be zero and then, by equation (5), K' or l would have to be infinity. Since K' has a finite value, the length would have to be infinity. To avoid this difficulty imagine the value of l to be adjusted so that K' equals unity. Then $-\log$ T = 1 or T $= \frac{P_2}{P_1} = \frac{1}{10}$. Under these conditions K' appears as that coefficient the value of which determines the distance, l, within which the radiant power is one-tenth extinguished, hence, "extinction coefficient."

As specified in their derivation, and as indicated by means of the subscript λ, equations (5) and (6) are applicable only when the wave-length is specified. In practice very narrow bands of the spectrum are used. Using these narrow bands and determining at successive wave-lengths the specific transmissive indices we can chart so-called absorption curves. (See figs. 20 and 24.) For regions of the spectrum in which the wave-length is lower than the wave-length of visible radiant energy photographic methods are employed. For regions in which the wave-length is larger than the wave-length of visible radiant energy thermoelectric methods are used. Undoubtedly the most fundamental data will be obtained when indicators are examined with radiant energy of a wide range of wave-length, but the immediate task is to make use of visible radiant energy.

SPECTROPHOTOMETERS

A brief description of a remarkably direct-reading instrument, the Keuffel and Esser Color Analyser, will show how the transmittance of a solution may be measured. Figure 21 is a diagrammatic representation of the instrument. See Keuffel (1925).

Radiant energy from tungsten lamps, 12, in the "integrating" sphere, 1, is diffusely reflected from two blocks of magnesia held

at 6 and 7.   The two beams of radiant energy pass through the slit 17 of the collimator, and are brought by the collimator to the prism 19.   The position of this prism, which can be rotated by the drum with wave-length scale 4, determines the narrow band of the spectrum in the photometric field at the eye-piece 21.   By means of the biprism 20 placed over the lens 18, there is produced the photometric field of the type illustrated by 9.   The energy in one-half of this field comes by one of the beams and that in the other comes by the second beam.

1. Spherical Light Source.
2. Photometer.
3. Spectromter.
4. Wave Length Scale.
5. Photometer Scale.
6. Holder for Standard Sample.
7. Holder for Reflection Samples.
8. Holder for Transparent Samples.
9. Field of View thru Eye Slit.
10. To Vacuum Ventilator.
11. Plug for Vacuum Ventilator
12. 400 Watt Lamps.
13. Lever for Raising Photometer.
14. Sector Discs.
15. Universal 110 Volt Motor.
16. Speed Control Rheostat.
17. Entrance Slit.
18. Collimator Objectives.
19. Dispersion Prism.
20. Bi-Prism.
21. Eye Slit.
22. Cast Aluminum Base.
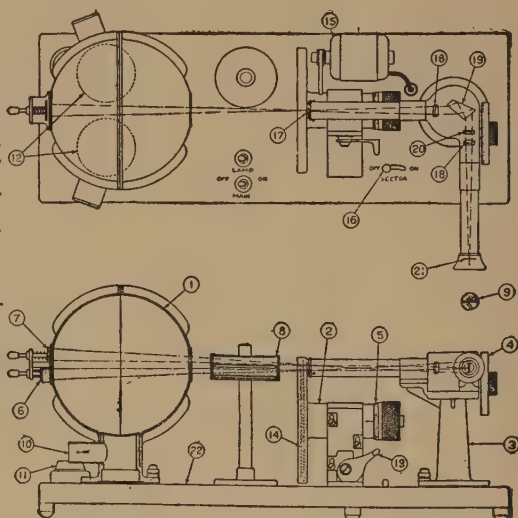
Diagram of K & E COLOR ANALYZER

FIG. 21

(Courtesy of Keuffel and Esser Company)

The one beam passes through the solution which is under examination and which is held at 8.   The other beam passes through a tube of the same length and similar glass end-plates (also held at 8) but containing the solvent alone.   The power in the given narrow section of the spectrum as seen at the eye-piece is now cut down by the rotating sector, 14, until photometric match is obtained.   The openings of the sector are controlled in an ingenious way while the sector is rotating.   The drum controlling these openings is so marked (scale 5) as to indicate directly the percentage transmission.

Since the transmission by the solvent and by the end-plates are compensated by placing in the path of the second beam a similar tube of like length and solvent, the percentage transmission observed is that of the solute, conditioned, of course, by the solvent.

The percentage transmission is one hundred times the transmittance T.

In some instruments the photometric match is obtained by altering the actual or virtual distances of two sources.

One of the most frequently used devices is the König-Martens photometer, the principal features of which are indicated by figure 22.
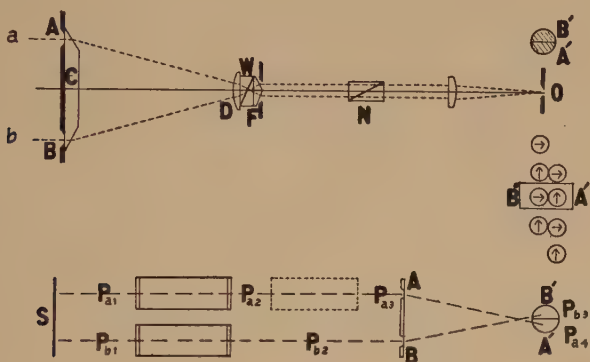
FIG. 22. (*Above*) PRINCIPAL FEATURES OF THE KÖNIG-MARTENS PHO-
TOMETER; (*Below*) ARRANGEMENT OF TUBES IN PHOTOMETER

Two beams of radiant energy coming through apertures A and B are to be reduced to equal power at the eye-piece O. The beams are converged by the biprism C to the collecting lens D and thence pass through the Wollaston prism W. The Wollaston prism is a crystal of calcite so cut as to separate the "ordinary" and "extraordinary" rays of the double refraction and deliver them polarized in planes mutually perpendicular. Each of the original beams, *a* and *b*, is thus divided into two and each of these is redivided by the biprism F. Thereby eight images corresponding to the two apertures A and B are formed. The polarization of each is indicated in the figure. All but one pair of these images is screened or absorbed by the walls of the instrument. In the pair selected the polarizations are in planes mutually perpendicular.

At N is a Nicol prism which can be turned.   At one position it
reduces to zero the amplitude of vibration in the ray that gives
image A'.   At 90° from this position it reduces to zero the
amplitude of vibration in the ray that gives image B'.

If the power at A equals the power at B and there are no inci-
dental polarizations at the surfaces of the optical parts, and if
there is no inequality of absorption in the paths, there will be
photometric match between A' and B' when the Nicol is turned
45° with relation to either of the extinction settings.

But assume that the radiant power at A is not equal to that
at B.   The angle at which the Nicol must be turned is related to
the ratio of the powers at A and B as follows:

Suppose beam a is polarized in the direction OA, figure 23.   Let
the amplitude of the vibrations be represented by the distance

Fig. 23

$\overline{OA}$. If the Nicol be turned so that its optic axis conforms to
OA it will not affect the amplitude.   If it be turned 90° from OA
it will reduce the amplitude of vibration in beam a to zero.   At
any angle θ the amplitude of the vibrations in beam a which
will be transmitted by the Nicol will be represented by the dis-
tance $\overline{OC}$.   Likewise for beam b the amplitude of the vibrations
transmitted by the Nicol will be $\overline{OD}$.

Geometrically we have

$$\overline{OC} = \overline{OA} \, \text{sine} \, \theta \qquad\qquad (7)$$

$$\overline{OD} = \overline{OB} \, \cos \theta \qquad\qquad (8)$$

or

$$\frac{\overline{OC}}{\overline{OD}} = \frac{\overline{OA}}{\overline{OB}} \tan \theta \qquad\qquad (9)$$

Again consider figure 22 in which the photometer with aper-
tures A and B is placed in train with the beams a and b which pass
through tubes of absorbing solution and solvent respectively.

For purposes of generality we shall assume that the light source, S, delivers to the absorbing tubes energy of unequal power P_{a1} and P_{b1}. For simplicity of exposition we shall imagine that the solvent and solution are held in like tubes of equal length. Also we shall imagine that the solute is removed from the solution tube and placed in a *space* of the same dimensions.

The various Ps in the figure represent the powers of the radiant energies at the several points.

The *ratio* of the powers of two beams equals the *ratio* of the *squares* of the amplitudes.

Therefore,

$$\frac{P_{a4}}{P_{b3}} = \frac{\overline{OC}^2}{\overline{OD}^2} \tag{10}$$

Photometric match is determined by adjustments to the condition that $P_{a4} = P_{b3}$. Using this relation and equations (9) and (10) we obtain

$$\frac{\overline{OB}^2}{\overline{OA}^2} = \tan^2 \theta \tag{11}$$

Since

$$\frac{\overline{OB}^2}{\overline{OA}^2} = \frac{P_{b2}}{P_{a3}},$$

$$\frac{P_{b2}}{P_{a3}} = \tan^2 \theta \tag{12}$$

The transmittance of the solute is given by:

$$T = \frac{P_{a3}}{P_{a2}} \tag{13}$$

The transmittance of the solvent is given by the identities

$$\frac{P_{a2}}{P_{a1}} \equiv \frac{P_{b2}}{P_{b1}} \tag{14}$$

Combination of equations (12), (13), and (14) yields:

$$\frac{P_{b1}}{P_{a1}T} = \tan^2 \theta \tag{15}$$

If no absorbents were in the train, $(T = 1)$, photometric match would be obtained at a new angle θ' of the Nicol in place of θ of equation (12) and the ratio $\dfrac{P_{b2}}{P_{a3}}$ would be replaced by $\dfrac{P_{b1}}{P_{a1}}$. Hence for the "zero setting" of the instrument

$$\frac{P_{b1}}{P_{a1}} = \tan^2 \theta' \qquad\qquad (16)$$

Substitute this in (15) and obtain:

$$T = \cot^2 \theta \times \tan^2 \theta' \qquad\qquad (17)$$

If the instrument conformed to the theory given above and if the light-source were such that $P_{a1} = P_{b1}$, (16) would become

$$1 = \tan^2 \theta' \qquad\qquad (18)$$

or

$$\theta' = 45°, 135°, 225° \text{ or } 315°.$$

If the instrument alter the amplitude of the vibrations in either ray by slight polarization at glass surfaces, it is equivalent to altering the relative powers P_{a1} and P_{b1}. Thus, for example, a "zero-setting" may occur at 46° instead of 45° even if $P_{a1} = P_{b1}$.

In (17) θ', it will be remembered, is the angle at "zero-setting" while θ is the angle with absorbents in train.

In case the tubes are reversed we have

$$T = \tan^2 \theta \times \cot^2 \theta' \qquad\qquad (19)$$

According to equation (17) or (19) the transmittance desired is determined as follows. First make photometric match with no absorbents in train. Read the angle θ'. Second make the reading with tubes of solvent and solution in train and read the angle θ. In each case the angle is that at photometric match.

It has been tacitly assumed that energy of one wave length or narrow spectral band has been used. The spectrometer delivering this to the eye is usually placed *beyond* the photometer. This virtually accomplishes the desired limitation.

For further information on spectrophotometers consult: Walsh (1926).
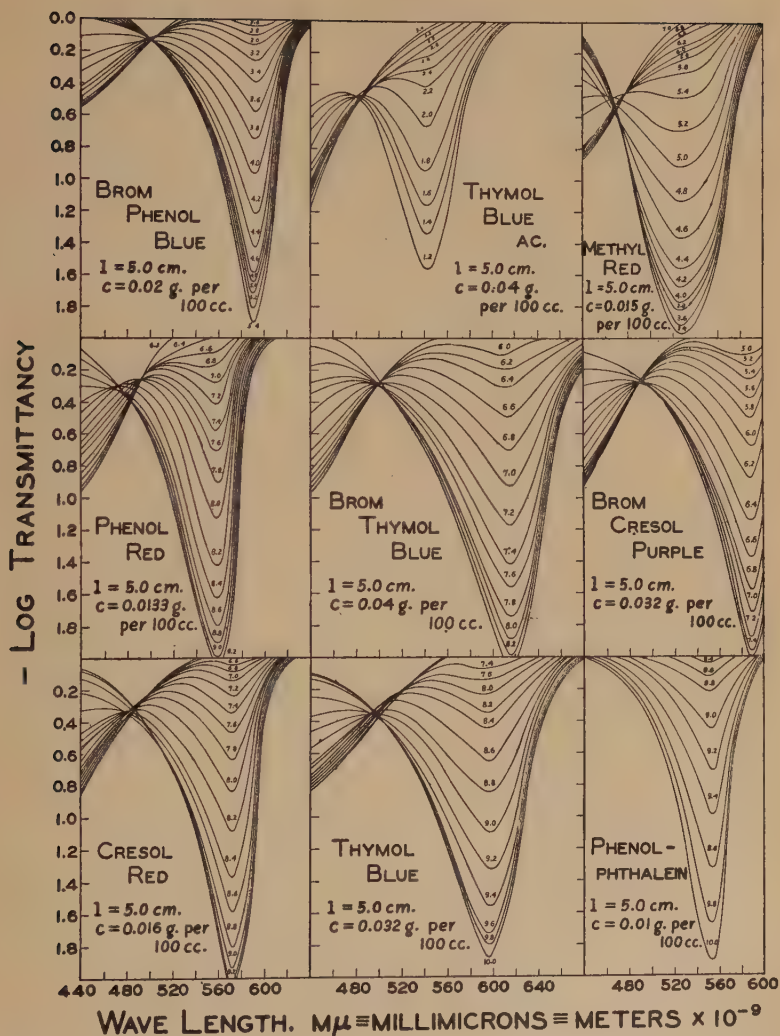
FIG. 24. ABSORPTION CURVES OF SEVEN SULFONPHTHALEINS, METHYL
RED AND PHENOL PHTHALEIN

(After Brode (1924))

ABSORPTION CURVES

By use of a spectrophotometer the value of a transmittance, T, or the value of $-\log T$ at any given wave-length or narrow section of the spectrum within the range of visibility is determined. When determinations are made at successive wave-lengths the results may be charted and a curve drawn through the points. Such a curve is called an absorption curve or a transmittance curve, according to the manner of charting, or choice.

Typical transmittance curves are shown in figure 24. Each curve represents the relation of $-\log T$ to λ, expressed in mμ, when the indicator was kept in a solution of the pH value indicated by the number. These curves were determined by Brode (1924). Each individual curve in figure 24 was determined while the solution was held at a constant value of pH by means of a buffer solution. In each instance the pH number is indicated. Any such curve can be called an "isohydric transmittance curve." Thiel, Dassler and Wülfken (1924) call them "isobathmen."

It is evident in figure 24 that the isohydric absorption curve changes in some regular way when the pH value of the indicator solution is changed. We naturally ascribe this to the change in the degree of dissociation of the indicator, and since the curve for a very low pH value is distinctly different from that for a comparatively high pH value we are led to attribute to the ion and to the undissociated molecule a qualitative difference in their abilities to absorb radiant energy.

According to equation (6) the effect of doubling the concentration c can be compensated by halving the length. Therefore, to make the argument simple, let it be imagined that all the ions are forced into the first half of the tube, and all the undissociated molecules into the second half. The final effect will be unchanged but we may now consider separately the transmission by the ions and by the undissociated molecules.

Let the radiant power incident at the first surface of the solution containing the ions be P_1 and that leaving this solution be P_2. Then up to this surface

$$\frac{P_2}{P_1} = 10^{-lc\alpha K_i}$$

where K_i is the molar transmissive index of the ions, c is the concentration of the *indicator* in the undivided solution, l is the length of the whole solution and α is the degree of dissociation. In the half of the divided solution c has been doubled but l has been halved $\left(\frac{1}{2} \, 2c \, \alpha \, = \, lc\alpha \right)$.

For the second part of the path of the radiant energy let P_3 be the radiant power leaving the solution of the undissociated molecules. Then

$$\frac{P_3}{P_2} = 10^{-lc\,(1-\alpha)\,K_u}$$

where K_u is the molar transmissive index of the undissociated molecules. The total transmittance equals $\frac{P_3}{P_1}$. Hence

$$- \log T = lc[\alpha K_i + (1 - \alpha) \, K_u] \qquad (20)$$

If $\alpha = 1$, $- \log T = lcK_i$. Thus, if the pH value of the solution is such as to cause complete dissociation, the observed transmittance is that of the ions alone and the measurable value of K_i at a given wave-length, or the absorption curve relating K_i to λ, becomes characteristic of the ions. Likewise, if $\alpha = 0$, $- \log T = lcK_u$; and now the isohydric absorption curve becomes characteristic of the undissociated molecules.

It frequently happens that *as the wave-length changes* in one direction the values of K_i and K_u approach and at some one value of λ become equal. Then by equation (20)

$$- \log T = lcK_i = lcK_u \qquad (21)$$

In (21) the degree of dissociation, α, does not appear. This means that each isohydric curve should pass through some common point as most of them are seen to do in figure 24. This point Thiel, Dassler and Wülfken (1924) call *"der isobestischer Punkt."* Prideaux (1926) adopts "isobestic point."

It may be noted that the isobestic point is not merely a point of intersection between the curve characteristic of the ions alone and the curve characteristic of the molecules alone, but that it is a point of intersection between all isohydric curves whatever the

value of the degree of dissociation.   Consequently the probability of its occurrence is low unless two "colored" components and two only have some intimate relation as have the ions and undissociated molecules in our equilibrium equation.

If then the instrumental accuracy of the spectrophotometric measurements be adequate to establish the actual rather than the apparent occurrence of an isobestic point, it would be presumptive proof that two absorbing components of the dye system and two only are related to the hydrion concentration of the solution, within the range of pH where the point suffers no displacement.

Not infrequently there are to be observed, in the published charts and tables of indicator absorption data, indications that there is a true isobestic point for a *limited range* of pH values but that an extreme change of pH throws the absorption curve out of conformity.   This suggests the formation of a new absorbing species.   If so, nonconformity to the isobestic point should be used as a warning that the argument to follow should be modified, and that, in the spectrophotometric method of determining pH values, on isohydric curves that do not conform to the isobestic point are to be avoided.

SPECTROPHOTOMETRIC DETERMINATION OF DISSOCIATION CONSTANTS

Let it be assumed that equation (20) is applicable.   Let the pH value of the solution be changed in one direction until the values of $-\log T$ no longer change.   It is then to be presumed that α has become either 1 or 0, according to the acidic or basic nature of the indicator and the direction of the change in pH.   Let the pH value of the solution now be changed in the other direction until the values of $-\log T$ no longer change.   It is of course impossible to tell from the spectrophotometric measurements whether an acidic or a basic indicator is being used but, as indicated in Chapter I, the data in either case can be treated as if for an acid.   Inspection of the absorption curves for the dissociated and undissociated indicator shows whether or not there is a wave-length at which either K_i or K_u, as it appears in equation (20), is negligible.   This wave-length should be as near as practicable to the peak of the curve for the chosen species, provided that it does not depart far from the region of good visibility,

presently to be discussed.   Let us assume that the ion is the chosen species and that the wave-length is such that (20) approximates closely to

$$- \log T = lc\alpha \, K_i \qquad\qquad (22)$$

Determine $- \log T$ when it is certain that the alkalinity of the solution is sufficient to make α practically unity.   Then $- \log T_m = lcK_i$, at a specific value of λ where T_m indicates minimum transmittance (maximum absorption).   Now change the pH value of the solution till it is within that range where α lies between 0.9 and 0.1; and, having measured the pH value of the well-buffered solution without the indicator, determine (for the same wave-length previously used) the new value of $- \log T$.   This will be designated by $- \log T_x$.   Then

$$\alpha = \frac{- \log T_x}{- \log T_m} \qquad\qquad (23)$$

In some cases it contributes to accuracy of measurement if the concentration or the tube length is varied.   In that case there can be used the equivalent of equation (23), namely:

$$\alpha = \frac{l_m \, c_m K_i}{l_x c_x K_i} \frac{\log T_x}{\log T_m} \qquad\qquad (24)$$

Remembering that we are using one wave-length, we can cancel K_i from equation (24).   Also the exact concentrations c_m and c_x need not be known if the ratio be known.

The values of α having been determined in a number of cases, there is used the familiar equation

$$pH = pK + \log \frac{\alpha}{1 - \alpha}$$

pH values being known from the buffers used, pK is now calculated.

Holmes (1924) uses the transmittances of both ion and undissociated molecules in the following manner.   Select two wave-lengths λ_1 and λ_2, preferably in regions of good visibility, one preferably near the peak of the curve for the ion and the other preferably near the peak of the curve for the undissociated mole-

cule. If it happens that these wave-lengths are such that in one case $K_{i\lambda 1} = 0$ and in the other case $K_{u\lambda 2} = 0$, equation (23) will apply to the ions and a similar equation will apply to the undissociated molecules. To distinguish the cases the subscripts $_{i\lambda 1}$ and $_{u\lambda 2}$ will be used with obvious meanings.

$$\alpha = \frac{[\log T_x]_{i\lambda 1}}{[\log T_m]_{i\lambda 1}} = R_i \tag{25}$$

$$1 - \alpha = \frac{[\log T_x]_{u\lambda 2}}{[\log T_m]_{u\bar\lambda 2}} = R_u \tag{26}$$

pK is found directly from the relation:

$$pH = pK + \log \frac{R_i}{R_u} \tag{27}$$

As Holmes (1924) notes, the change in the concentrations of the ions and the ionogen both contribute to the ratio $\dfrac{R_i}{R_u}$ and consequently the use of this ratio is preferable, where practicable.

In case there cannot be selected a wave-length at which the absorption is due practically to the ion or the ionogen alone, equation (20) must be used. The resulting equations for α by either of the above principles becomes somewhat more complicated (cf. Vlès, 1925), but this in itself is not serious. The real difficulty lies in the accurate estimation of K_i and K_u which can no longer be eliminated. The determination of a transmissive index requires a pure compound used in known concentration. If the pure compound is not available the apparent transmissive indices must be determined.

SPECTROPHOTOMETRIC DETERMINATION OF pH

There is to be used the equation:

$$pH = pK + \log \frac{\alpha}{1 - \alpha}$$

The value of α is to be determined by the ratio $\dfrac{\log T_x}{\log T_m}$ where T_x is the transmittance of the tested solution containing the

indicator partially transformed and T_m is the transmittance of the indicator fully transformed. Therefore pK must have been previously determined by the method described in the previous section and by the use of buffers which now become the standard of reference. See table 25.

TABLE 25

pK values and absorption maxima of sulfonphthaleins

A = solution used for full transformation.

Solutions: 1. Between 20 and 36 per cent HCl.

        2. M/20 borax.

        3. M/2 trisodium phosphate.

Formulas: a. $pH = pK - \log \dfrac{\alpha}{1-\alpha}$.

         b. $pH = pK + \log \dfrac{\alpha}{1-\alpha}$. $\alpha = \dfrac{\log T_x}{\log T_m}$.

Standards of reference: Clark and Lubs' buffer solutions.

INDICATOR	pK	WAVE-LENGTH OF MINIMUM TRANSMITTANCE	A	FOR-MULA
m-cresol purple (acid range)............	1.51	533 (Cohen)	1	a
Thymol blue (acid range).............	1.5	544 (Brode)	1	a
Brom chlor phenol blue..............	3.98	596 (Cohen)	2	b
Brom phenol blue....................	4.10	592 (Brode)	2	b
Brom cresol green...................	4.68	614 (Holmes)	2	b
	4.67	617 (Cohen)		
Chlor cresol green...................	4.8	612 (Cohen)	2	b
Chlor phenol red.....................	5.98	573 (Cohen)	2	b
Brom phenol red.....................	6.16	574 (Cohen)	2	b
Brom cresol purple...................	6.3	591 (Brode)	2	b
Brom thymol blue....................	7.0	617 (Brode)	3	b
Phenol red..........................	7.9	558 (Brode)	3·	b
Cresol red...........................	8.3	572 (Brode)	3	b
m-cresol purple (alkaline range).......	8.32	580 (Cohen)	3	b
Thymol blue (alkaline range)........	8.91	596 (Holmes)	3	b
	8.90	596 (Brode)	3	b

Establish by trial that strength of the standard indicator solution which, with the tube length selected, will give a transmittance of 0.2–0.1, when the indicator is fully transformed to the "alkaline" (or, if preferred, to the "acid") form. Establish accurately the value of $\log T_m$. Then with the *same* indicator

solution added in the *same* proportion to the tested solution determine log T_x. Introduce the values into the above equation and with the given value of pK solve for pH. To facilitate such calculations there is given in Appendix F (page 677) values of log $\frac{\alpha}{1-\alpha}$ for various values of α.

There can be used also the $\frac{R_1}{R_u}$ values as discussed in the previous section.

In table 25 are given the wave-lengths at which maximum absorption of several indicators are reported. It is well to select a wave-length near such a "peak." There might have been included the extinction coefficients for these stated wave-lengths. However, extinction coefficients are misleading in practical applications of the method because, to be of universal significance, they would have to apply to these rare articles of commerce— pure indicators. One hundred per cent purity of indicator and perfection in the construction of a standard solution of known concentration cannot always be depended upon and, as shown, are unnecessary to the method when a wave-length can be selected at which the equations permit the elimination of one or the other extinction coefficient.

For the production of the full transformation of the indicator the same precautions must be used that are applied in the Gillespie method. Data for the sulfonphthaleins are found in table 14 (page 122).

A fundamental assumption in the method as described is that the specific absorptive property of the ion and of the ionogen are not affected by change in the general composition of the solution, e.g., alteration of "salt" content by addition of neutral salt or change in buffer composition. That this assumption is not justified in strictness is shown by Halban and Ebert (1924).

Of the method, Holmes (1924) remarks:

"With judicious selection of indicators and technique the spectrophotometric method affords the maximum accuracy possible in indicator methods. . . . . The phenomena of dichromatism, encountered with many indicators, introduce no interference. The presence of such degrees of color and turbidity as are ordinarily met in solutions to be evaluated does not affect the accuracy with which the ratios may be measured,

since the technique of spectrophotometric practice is, or may be made, such that an exact compensation for their effects is obtained automatically. The difficulties introduced by excessive color or turbidity may be overcome by increasing the concentration of the indicator and decreasing the thickness of the layer of solution employed in the measurements. The resort to thin layers of solution should also render it possible to determine the ratio of a solution when only a few drops of material may be available for examination.''

A fuller discussion of the effect of turbidity would be welcome. In passing it is well to note how well the values of α, determined spectrophotometrically, conform to the type curve corresponding to the simple equation

$$pH = pK + \log \frac{\alpha}{1 - \alpha}$$
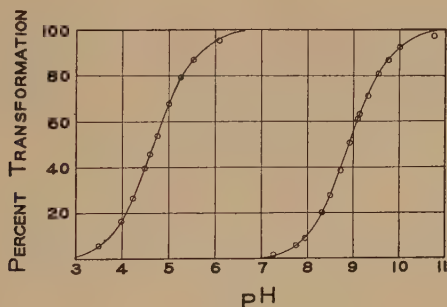
FIG. 25. RELATION OF pH TO PER CENT TRANSFORMATION OF BROM CRESOL GREEN (pK = 4.68) AND OF THYMOL BLUE (pK = 8.91)
(After Holmes and Snyder (1925))

Determinations by Holmes and Snyder (1925) are shown in figure 25.

Other references to the use of spectroscopy in indicator work are: Birge and Acree (1919), Baker and Davidson (1922), Bruére (1925), Henri and Fromageot (1925), Hildebrand (1908), Buch (1926), Lund (1927), Moir (1916), Morton and Tipping (1925), Paulus, Hutchinson, and Jones (1915), Prideaux (1925), Siegler-Soru (1927), Stenström and Reinhard (1925), Vlès et al. (1922–1927). Adams and Rosenstein (1914), Brightman et al. (1918–1920), Hirsch (1925).

EFFECTS OF ABSORPTION ON THE STIMULUS AS IT REACHES THE EYE

Transmittance, is merely the fraction $\dfrac{P_2}{P_1}$, the fraction of the power incident at the surface 1 which emerges at the surface 2. It has been particularly noted that this fraction varies with the

TABLE 26

Relative visibility of radiant energy of different wave length and spectral distribution of relative radiant energy for standard white light

WAVE LENGTH	RELATIVE VISIBILITY*	RELATIVE RADIANT ENERGY— STANDARD WHITE LIGHT†	WAVE LENGTH	RELATIVE VISIBILITY*	RELATIVE RADIANT ENERGY— STANDARD WHITE LIGHT†
$m\mu$			$m\mu$		
400	0.0004	53.33	550	0.995	100.95
410	0.0012	60.00	560	0.995	100.00
420	0.0040	66.67	570	0.952	99.05
430	0.0116	69.52	580	0.870	97.14
440	0.023	77.14	590	0.757	95.24
450	0.038	86.19	600	0.631	94.29
460	0.060	92.38	610	0.503	93.33
470	0.091	96.19	620	0.381	92.38
480	0.139	99.05	630	0.265	91.43
490	0.208	100.48	640	0.175	90.48
500	0.323	100.95	650	0.107	89.52
510	0.503	101.43	660	0.061	87.62
520	0.710	100.95	670	0.032	86.19
530	0.862	100.95	680	0.017	84.29
540	0.954	100.95	690	0.0082	82.86
			700	0.0041	80.48

* Provisionally adopted by the International Commission on Illumination, Geneva, July, 1924. See Gibson *et al.* (1925).

† Average noon sun at Washington. Used as standard white. See Gibson *et al.* (1925).

wave-length. It must now be emphasized that the values of the incident power at different wave-lengths vary with the source. In table 26 are shown relative intensities at different wave-lengths of the radiant energy of white light. The values given are proportional to the relative powers. By means of the relative

value of P_1 and the value of the fraction $\frac{P_1}{P_2}$ (i.e., T) there can now be calculated the value of P_2 for any wave-length. P_2, as evaluated in relative terms, is the destined stimulus as it leaves the solution on its way to the eye.

Now the visibility of radiant energy varies greatly with the wave-length. Standard values of relative visibility provisionally adopted in 1924 by the International Commission on Illumination as quoted by Gibson *et al.* (1925) are shown in table 26. The product of the relative visibility and the relative value of P_2 at a given wave-length is the relative light or the luminosity for the wave-length under consideration.

At this point attention may be called to our previous avoidance of the word "light." It is a word which is in such common use that no committee can ever dictate its good and proper usage. Yet, in an exposition of such technical matters as those now under discussion there is a distinct advantage in adhering to the nomenclature of the Colorimetry Report (Troland, 1922) wherein the physical aspects of radiation are kept distinct from physiological effects. There it is stated, that *light* is to be regarded as a "Psycho-physical" quantity. It is defined "as the product of absolute power and visibility measures for any given sample of radiant energy."

"*Relative* light quantities are called *luminosities.*"

The only immediate concern which we have for luminosity, *in the application of the spectrophotometer* is that the luminosity shall be sufficient to make possible accurate measurements in which the eye is the detector of inequalities. On the other hand, further consideration of this quantity reveals relations of considerable importance to the *direct visual* observation of indicator solutions. An instance of this will be shown in the next section.

DICHROMATISM

Consider for instance a solution of brom cresol purple which at pH 7.6 gives the transmittance curve indicated in figure 24. By means of the data of table 26 and the values of T read from a large scale drawing of figure 24 there are calculated and plotted as curve A of figure 26 the variation of luminosity with wave-

length. Now let either the concentration or the length of the
brom cresol purple solution be increased ten times and for the
new condition let there be plotted curve B.

In the first case (low concentration, or short tube), the luminos-
ity is greatest in the "blue" and "blue-green."   There is still a
marked luminosity in the "red."   The combined effect is "purple."
In concentrated solution or deep layers as shown by curve B there
is very little luminosity for the "blue" and the luminosity for the
"red" is dominant.   The effect approaches "red."   Thus a change
of concentration or length causes a distinct change of color.   This
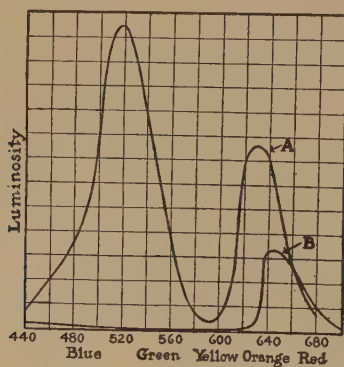
FIG. 26. LUMINOSITY CURVES, CALCULATED BY MEANS OF THE TRANS-
MISSION, THE RELATIVE RADIANT ENERGY OF STANDARD WHITE
LIGHT AND THE RELATIVE VISIBILITY

Curve A—brom cresol purple in dilute solution.   Curve B—brom cresol
purple in ten times the concentration of case A.

is called "dichromatism."   It can readily be observed with the
proper concentration of brom cresol purple by observing it in a
test tube, first sidewise and then lengthwise of the tube.   It is
of very great importance in the determination of pH values.   In
the first place, two solutions of like pH value containing brom
cresol purple will give distinct differences in "color" *quality* if
there is an error either in the concentration of indicator or in the
depth of view.   Secondly, if a solution containing suspended
material be compared with a clear standard, an error may arise
from the fact that in the turbid solution much of the radiant energy
reaching the eye may not have traversed the whole depth but

may have entered from the side and having been scattered by the particles may have traversed only a shallow layer of the solution. Indeed turbid solutions containing this indicator often appear "bluer" than the standard having the same pH value and having the same concentration of the indicator. With milk the red tone of brom cresol purple is almost undetectible unless reflected light be screened off.

This effect, dichromatism, is operative to some extent with most indicators but it becomes distinctly troublesome only with indicators such as brom cresol purple, and brom phenol blue, the absorption curves of which are located in such a position that effective amounts of radiant energy are transmitted in the region of visible "red" on the one hand and visible "blue" on the other hand.

Since the luminosity is determined in part by the spectral distribution of the relative power of the source, the luminosity at a given wave-length will vary with the source. Artificial illuminants, as, for instance, the tungsten lamp furnish radiant energy the power of which at different wave-lengths is much less uniform than that of sunlight. Such illuminants are commonly described as deficient in "blue" or relatively rich in "red." Thus a dichromatic indicator appears much "redder" under a tungsten lamp than in daylight.

In dealing with dichromatic indicators which give trouble in direct visual observations, it sometimes helps to change the source of illumination. For instance, it is an appreciable although not an entirely satisfactory aid in the use of brom cresol purple to screen off the "blue" in the source of illumination. This can be done crudely as follows. In an ordinary box of convenient size are mounted three or four large electric lights. A piece of "tin" serves are reflector. The box may be lined with asbestos board. A piece of glass, cut to fit the box, is held in place on one side by the asbestos lining and on the other by a few tacks. This glass serves only to protect the screen and is not essential. The screen is made from translucent paper known to draughtsmen as "Economy" tracing paper. It is stretched across the open side of the box and painted with a solution consisting of 5 cc. of 0.6 per cent phenol red and 5 cc. of $\frac{M}{5}KH_2PO_4$ (stock standard phosphate

solution). While the paper is wet it is stretched and pinned to the box with thumb tacks. If a dark-room is not available for observations, exterior light may be shut off with a photographer's black cloth.

Blue-yellow indicators which retain a dichromatic red may be observed by mercury arc. Its emission is poor in "red" but "yellow," "green" and "blue" lines fall in the spectrum where, for instance, shifts in the absorption bands of brom phenol blue occur.

The absorption spectra of all the indicators of the sulfon phthalein series are such that the appearance of dichromatism must be expected under certain conditions. It will be observed with phenol red in illumination relatively poor in "red" and rich in "blue," for example, that of a mercury arc; and with thymol blue in illumination relatively poor in "blue" and rich in "red" for example, ordinary electric light.

OBSERVATIONS BY THE COLOR-BLIND

Curiously enough the author never has heard this problem discussed until he raised the question himself, a fact which suggests that few people have such insuperable difficulties with the indicator method that they are conscious of possible personal limitations. It may be said at once that an adequate discussion of this problem would require a clear recognition of the various types of color-blindness and that the author is not competent to deal with the subject except superficially. One aspect is clear. The physical phenomena are definite. The absorption bands are usually broad enough so that some alteration with change of pH occurs at wave-lengths at which eyes of limited deficiencies are still sensitive. Consequently, changes are detected. It is a matter of no fundamental importance that the deficiencies lead to wrong *names* of *colors*. The serious aspect is deficient sensitivity in the region of greatest indicator change. When this occurs there may be manifest (in certain instances) avoidance of red-yellow indicators and preference for blue-yellow indicators or *vice versa* (compare Saunders (1923)). Preferences arising from real physiological deficiencies and not from esthetics deserve more study. Such problems became important when, as frequently happens in industrial work, extensive measurements become

routine and rapidity, accuracy and ease of measurements should be encouraged.

DIFFERENTIATION BY EYE

Let us also consider the range of an indicator as it is determined by the differentiating power of the eye. An approximate treatment of this is all that will be attempted.

Use the equation:

$$pH = \log \frac{1}{K} + \log \frac{\alpha}{(1 - \alpha)}$$

On differentiation the rate of increase in α with increase of pH is found to be:

$$\frac{d\alpha}{d(pH)} = 2.3 \, \alpha \, (1 - \alpha).$$

When

$$\frac{d^2\alpha}{d(pH)^2} = 0, \alpha = \frac{1}{2},$$

In other words the maximum rate of increase in dissociation is at the half transformation point. This fixes a reference point when indicators are to be employed in distinguishing differences in pH. The question now arises whether or not this is the central point of the optimal conditions for differentiation of pH values. It may be said at once that it is not, because the eye has not only to detect differences but also to resolve these differences from the color already present. Experience shows that the point of maximum rate of increase in α is near one limit of the useful range and that this range lies on the side of lower color. Thus, in the case of the one-color indicator phenolphthalein, the useful zone lies between about 8.4 and 9.8 instead of being centered at 9.7 which corresponds with the point of half-transformation. In the case of a two-color indicator such as phenol red the same reasoning holds, because the attention fixes upon the very dominant red. With other two-color indicators the principle holds except when there is no very great difference in the command upon the attention by one or the other color.

It should be mentioned however that these more or less empiri-

cal relations are observed in comparing colors at equal incre-
ments of pH when the indicator concentration is adjusted to
emphasize the differences among the less intensely colored tubes.
By suitable dilution of the indicator the differences among the
tubes having the higher percentage color may be emphasized
and the useful range of the indicator slightly extended.   In prac-
tice this is a procedure which requires care for it is easy to be-
come confused when dealing with different concentrations of the
same indicator.

The fixing of the lower pH limit of usefulness of a given indi-
cator involves another factor.   There is the question of the total
indicator which may be brought into action.   A dilute solution
of phenolphthalein may appear quite colorless at pH 8.4 while
a much stronger solution will show a distinct color which would
permit distinguishing 8.2 from 8.4.   But the concentration is
limited by the solubility of the indicator and this must be
taken into consideration.   In short there is no basis upon which
to fix definite limits to the pH range of a given indicator, and
those limits which are given must be considered to be arbitrary.
On the other hand the apparent dissociation curve is quite defini-
tive; and were it not for the greater convenience of the "range of
usefulness" it would be preferable to define the characteristics
of an indicator in terms of its apparent dissociation constant.

COLOR

Translation of the data of transmittances into luminosities
requires the data of table 26.   But if an attempt is made to carry
the matter further into a description of the psychological affair
called *color*, additional data are required.   This is beyond the
scope of this treatise, and since it is we have taken liberties in
preceding paragraphs and have named stimuli by the names of
the effects, e.g., "red."

In no part of our subject is color *quantitatively* evaluated.   As
we shall see presently the ordinary *colorimeter* is misnamed.

On the other hand, when we use two-color indicators like the
sulfonphthaleins, and have normal eyes, we undoubtedly utilize
color distinction, which stands us in good stead and often becomes
the sole criterion of distinctions when turbidity and other factors
interfere with the judgment of relative *intensities*.   See also

page 131 on the utilization of color-quality in observations of "one-color" indicators.

THE "COLORIMETER," I.E., COMPARATOR

Beer's law is:

$$- \log T_\lambda = lcK_\lambda$$

(see page 144) where T is the transmittance at a specified wave-length, λ, l is the length of the absorbing layer, c is the concentration of absorbing substance and K_λ is a constant characteristic of the absorbing substance for the specified wave-length λ. The transmittance is the ratio, $\dfrac{P_2}{P_1}$, of the power of the radiant energy emerging from the solution to the power incident at the first surface.

Imagine two solutions receiving from a source the same radiant power P_1 at wave-length λ and containing a substance characterized by the absorption constant K_λ. Let the length l of one solution or its concentration c, of absorbing material, be adjusted until the emergent power P_2 is equal to that of the second solution. The transmittances will be equal in each case. Then by applying the above equation to the two cases, indicated by subscripts 1 and 2, and solving, we have:

$$- \log T_x = l_1 c_1 K_x = l_2 c_2 K_x; \text{ whence: } l_1 c_1 = l_2 c_2$$

or

$$\frac{c_1}{c_2} = \frac{l_2}{l_1}$$

The ordinary "colorimeter" of the Duboscq type is a device whereby the length of absorbing layers l_1 and l_2 can be varied and measured, until, by an optical device for bringing the photometric fields into juxtaposition it is seen that the transmittances are equal. If c_1 is known, and the ratio $\dfrac{l_2}{l_1}$ is measured, c_2 is determined.

In the treatment given above, it was tacitly assumed that absorption by the solvent could be neglected. This assumption is not serious. The specification that there is to be used radiant energy of one wave-length ("monochromatic light") is, of course,

not usually met.   And yet it is essential to the *strict* applicability of the laws involved.   We need not repeat here the discussion, given in a previous section, of the variation in "color-quality" made very evident in solutions of "dichroic" indicators as the concentration of indicator or the length of absorbing layer is varied.   Suffice it to say, that if a "colorimeter" is used with two-color indicators, the variation in "color-quality" with variation in the ratio of tube lengths will be so disconcerting as to make the use of the ordinary "colorimeter" quite useless for pH measurements.

Gillespie (1921) brought into prominence a principle which promises to be of considerable value.   It is illustrated diagrammatically by figure 27.   The vessels A, B, C and E are of colorless glass.   The bottoms should be optically plane-parallel.   A and C are fixed while B may be moved up or down.   The position of
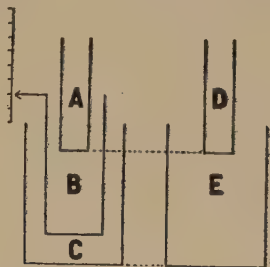
Fig. 27. Diagrammatic Section of Gillespie's Color Comparator

B is indicated on a scale the zero mark of which corresponds to the position of B when B and C are in contact and the 100 mark of which corresponds to the position of B when B is in contact with A.   If now there is placed in B a solution of the acid form of an indicator and in C a solution of the same concentration of the indicator transformed completely to the alkaline form, it is obvious that the position of the vessel B will determine the ratio of the two forms of the indicator which will be within the view.

For comparison a solution to be tested is placed in E together with that concentration of indicator that occurs in the optical system B-C.   For colored solutions tubes A and D are used as in the Walpole system, which will presently be described.   As Gillespie has indicated, this "colorimeter" should be useful for certain general work where the exact principles of color comparison have often been neglected.

A - eye point
B - eyepiece
C - prism
D - plunger
E - cups, movable separately
F - cups, movable together
G - stoppers
H - auxiliary cups
R - reflector
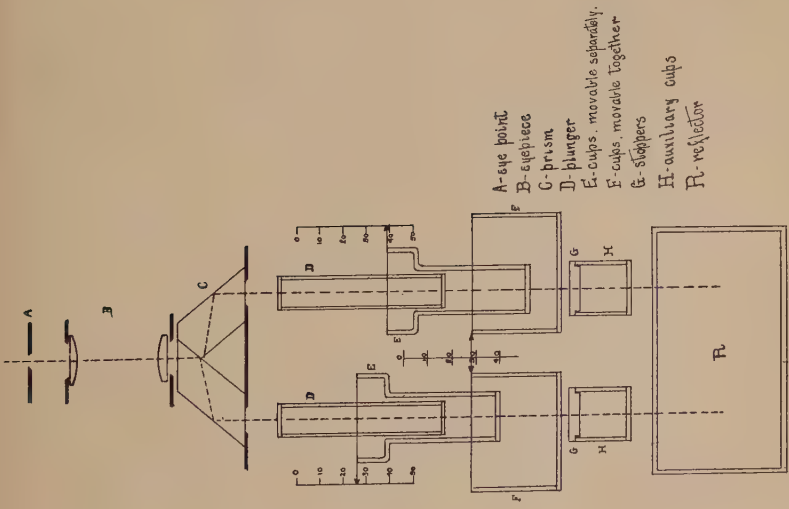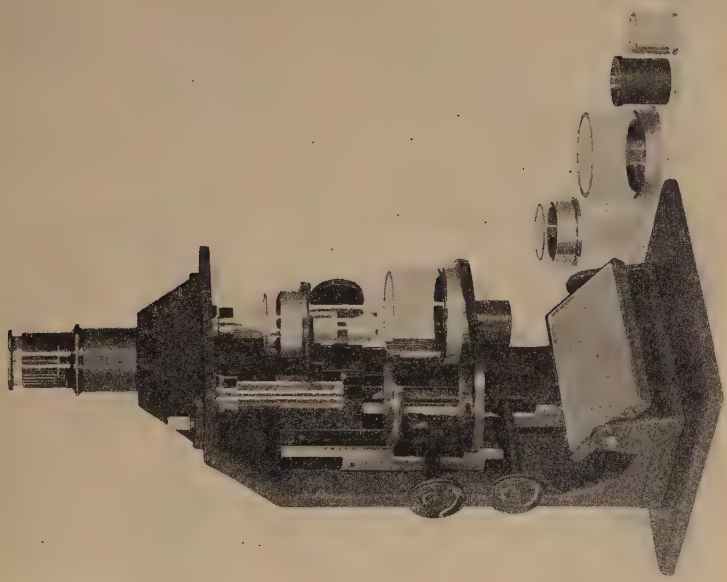
Fig. 28b

Fig. 28a

Fig. 28. Schema and Photograph of Compensation Color Comparator
(Courtesy Bausch and Lomb Optical Company)

An instrument embodying the principle which Gillespie used was described by Mines (1910) under a title concerning the action of beryllium, etc., on the frog's heart. Wu (1923) and Gerretsen (1924) have employed the principle. The instrument made by the Bausch and Lomb Optical Company for Dr. A. B. Hastings is shown in figure 28. It has the advantage of auxiliary cups H useful in the compensation of natural colors of solutions.

<div align="center">COLOR-WEDGE</div>

Another principle which has been put to use is embodied in the "color-wedge" of Bjerrum (1914). This is a long rectangular box with glass sides and a diagonal glass partition which divides the interior into two equal wedges. One compartment contains a solution of the indicator fully transformed into its alkaline form, the other a like concentration of the indicator transformed to the acid form. A view through these wedges should imitate the view of a like depth and concentration of the indicator transformed to that degree which is represented by the ratio of wedge thicknesses at the point under observation. Compare Barnett and Barnett (1921) and Myers (1922). Myers apparatus has been developed commercially and is now on the market. Wherry has reproduced Bjerrum's color-wedge with celluloid walls and made of it a very helpful field kit.

McCrae (1926) Kolthoff (1924) have also employed the wedge principle.

In the use of the wedge the relation between wedge thicknesses and pH values are determined by the relation

$$pH = pK_a + \log \frac{\text{thickness 1}}{\text{thickness 2}}$$

provided, of course, the indicator has been properly used.

<div align="center">COMPENSATION FOR NATURAL COLOR OF A SOLUTION</div>

There have been two chief methods of dealing with the interfering effect of the natural color of solutions. The first method, used by Sørensen (1909), consists in coloring the standard comparison solutions until their color matches that of the solution to be tested, and subsequently adding to each the indicator.

Sørensen's coloring solutions are the following:

a. Bismarck brown (0.2 gram in 1 liter of water).
b. Helianthin II (0.1 gram in 800 cc. alcohol, 200 cc. water).
c. Tropaeolin O (0.2 gram in 1 liter of water).
d. Tropaeolin OO (0.2 gram in 1 liter of water).
e. Curcumein (0.2 gram in 600 cc. alcohol, 400 cc. water).
f. Methyl violet (0.02 gram in 1 liter of water).
g. Cotton blue (0.1 gram in 1 liter of water).

The second method was introduced by Walpole (1910). It consists in superimposing a tube of the colored solution over the standard comparison solution to which the indicator is added, and comparing this combination with the tested solution plus indicator superimposed upon a tube of clear water.

THE BLOCK COMPARATOR

A somewhat crude but nevertheless helpful application of Walpole's principle may be made from a block of wood. Six deep holes just large enough to hold ordinary test tubes are bored parallel to one another in pairs. Adjacent pairs are placed as close to one another as can be done without breaking through the intervening walls. Perpendicular to these holes and running through each pair are bored *smaller* holes through which the test tubes may be viewed. The center pair of test tubes holds first the solution to be tested plus the indicator and second a water blank. At either side are placed the standards colored with the indicator and each backed by a sample of the solution under test.
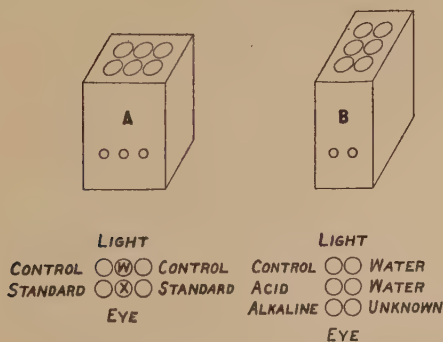
FIG. 29. SIMPLE COMPARATORS

This is the so called "comparator" of Hurwitz, Meyer, and Ostenberg (1915). Before use it is well to paint the whole block and especially the holes a non-reflecting black. To produce a "dead" black use a soft wood and an alcohol wood-stain.

This comparator is shown in two forms in figure 29. Form A is used with the unknown X + indicator, backed by a water blank, W, in the center. On either side is placed the standard buffer + indicator, backed by a tube of the unknown (control) to compensate for the natural color or turbidity of the unknown. Form B is used with the Gillespie method. The unknown + indicator is backed by two tubes of water. The acid solution of indicator and the alkaline solution of indicator are backed by a tube of the untreated unknown (control) to compensate for the natural color or turbidity of the unknown.

There have been described many elaborations of this simple device. Several provide mechanical means of rapidly exchanging tubes in the field of view, see for example Cooledge (1920).

In the operation of this comparator with "one-color" indicators (nitrophenols) Michaelis uses a screen of blue glass. See page 131.

COMPENSATION FOR TURBIDITY

Turbidity often presents a difficult problem. Sørensen (1909) has attempted to correct for this effect by the use of a finely divided precipitate suspended in the comparison solution. This he accomplishes by forming a precipitate of $BaSO_4$ through the addition of chemically equivalent quantities of $BaCl_2$ and Na_2SO_4. Strictly speaking, this gives an imperfect imitation, but like the attempt to match color it does very well in many instances. The Walpole superposition method may be used with turbid solutions as well as with colored, as experience with the device of Hurwitz, Meyer and Ostenberg has shown. In passing, attention should be called to the fact that the view of a turbid solution should be made through a relatively thin layer. When the comparison is made in test tubes, for instance, the view should be from the side.

There are some solutions, however, which are so dark or turbid that they cannot be handled with much precision by any of these methods. On the other hand a combination of these methods with moderate and judicious dilution [as was indicated in Chapter II this may not seriously alter the pH of a solution], permits

very good estimates with solutions which at first may appear "impossible." Some of the deepest colored solutions permit reasonably good determinations and when sufficiently transparent permit the application of spectrometric devices. Turbidity on the other hand is sometimes unmanageable. Even in the case of milk where comparison with a standard is out of the question a two colored indicator presents a basis for judgment. See also page 136.

REFLECTIONS

Buckmaster (1923) has suggested using films of tested solution and of buffer standards. The comparison is to be made by *reflected light*. He does not describe the principles. Since they are rather complex and since the procedure seems not to be of immediate importance, the citation will suffice.

FLUORESCENT INDICATORS

A number of substances, among them fluorescein, not only suffer changes in the grosser aspects of their color in solution when the pH value of the solution passes through a certain range, but also fluoresce within and above one zone of pH and not below the zone.

True fluorescence is described as follows. Radiant energy of one or another wave-length is absorbed by the substance and the energy is given forth as radiant energy of another wave-length usually greater than that of the exciting radiation. Fluorescence is therefore best observed indirectly as if one were considering the substance the source. An extensive discussion is given by Pringsheim (1923) and Wood (1921).

Since, in some cases, there appears to be a direct relation between the degree of fluorescence and what might be expected to be the degree of dissociation as controlled by buffer solutions, measurement of the degree of fluorescence provides a method of measuring hydrion concentration. In figure 30 is a graph taken from the work of Desha, Sherrill and Harrison (1926) which shows the relation between the pH values of the solution and the degree of fluorescence of 2 naphthol, 3, 6-disulfonic acid. The fluorescence is very easily influenced by chlorides. Included in the paper mentioned above are data for other substances such as quinine.

See also Mellet and Bischoff (1926) and Robl (1926).
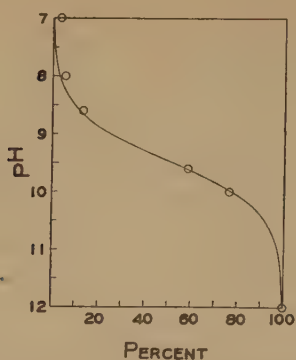
Fig. 30. Relation of pH to Per Cent Maximum Fluorescence of 2-naphthol,3,6-disulfonic Acid

Center of curve at pH 9.45. (After Desha, Sherrill and Harrison (1926))

ARTIFICIAL COLOR STANDARDS

There is an inherent simplicity in the use of standard buffer solutions and indicators themselves which would seem to preclude attempts to use artificial standards. And yet there seems to be an insistent demand for artificial standards. Even color charts are in demand! See page 65. These should be used with due precautions.

Grieg-Smith (1924) tells us that he makes his own water color standards for use with the spot-plate method and that he has seen similar standards at the Lister Institute. They can be prepared by a good artist better than by the printer's art. The original color chart which Professor Max Brödel did in water color for reproduction in the first edition of this book was a beautiful piece of work: but it could not be reproduced accurately and was used only as a guide. The artist's eye is not the eye of the spectrophotometer or of the camera or of the printer.

In the same category of *artificial* standards fall the organic or inorganic solutions such as those proposed or discussed by Haskins (1919), Kolthoff (1922), Risch (1924), Janke and Kropacsy (1926), Bruére (1926), Taub (1927), Jørgensen (1927). See also comments on inorganic standards by Breslau (1925).

Sondén (1921) has used colored glasses (see also Anon. (1927),

J. Sci. Inst. **4**, 327).   Incidentally it is interesting to note how the old Lovibond tintometer with its colored glasses has become quite out of date.

MIXED INDICATORS

Mixtures of indicators are employed for two very distinct purposes, only one of which justifies their description in this chapter.
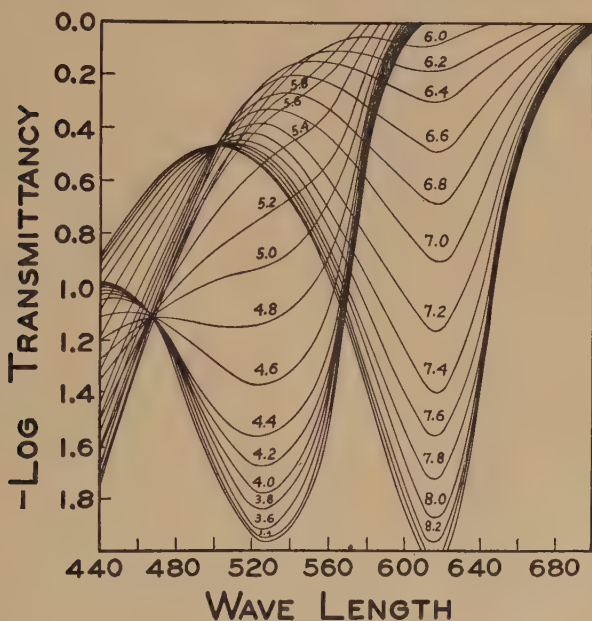
FIG. 31. ABSORPTION CURVES FOR THE MIXED INDICATOR: 0.015 GRAM
METHYL RED + 0.04 GRAM BROM THYMOL BLUE
(After Brode. (1924))

Sometimes a rational selection of indicators having different absorption bands or the admixture of an indicator with a dye which is not itself an indicator, results in color-changes more easily distinguished. A case in point is described by Hickman and Linstead (1922) who use xylene cyanole F F as an "internal light filter" in conjunction with methyl orange (1 part methyl orange to 1.4 part cyanole in 500 parts 50 per cent alcohol).   The result

at pH 3.8 is a grey intermediate color which, these authors claim, increases the ease of detecting end-points in titrations.   The absorption bands showing the rationale of the combination are given in the original paper.

For a very different purpose is admixture of indicators to extend with one test solution the range of pH values determinable. While recognizing some advantage in this, the author has never felt it to be a distinct advantage to ordinary pH measurements. In certain titrations the ability to detect two or more end-points widely apart on the pH scale is a distinct advantage of indicator mixtures.

A spectrophotometric analysis of one mixture is shown in figure 31.   This analysis by Brode (1924) illustrates a mode of attack which should be profitable in cases where specific results are to be achieved.

Several references to mixed indicators are given in Chapter IV.

PHOTOELECTRIC CELLS

Now that the photoelectric cell is coming into more general use it will doubtless be applied in a variety of ways in our subject. Reimann (1926) describes its use in titrations and Müller and Partridge (1927) apply it to the automatic control of titrations. The selenium cell has been applied by Hjort, Lowey and Blackwood (1924) in end-point work with indicators absorbing in the orange and red.   In following absorption in the ultra-violet certain types of photoelectric cell have been very useful.   See for instance Halban and Geigel (1920), Halban and Siedentorff (1922) and Kaplan (1927).   There may be rare instances when minute deflections of the galvanometer mirror in potentiometric measurements have to be detected.   The photoelectric cell has been used to amplify such minute deflections.

For a discussion of photoelectric cells as applied to colorimetry see Campbell and Gardiner (1925) and also the book on spectrophotometry by Walsh.

A series of judgments, revised without ceasing, goes to make up the incontestable progress of science.—DUCLAUX.

INTRODUCTION

There are errors of technique, such as incorrect apportionment of the indicator concentration in tested and standard solution and the use of unequal depths of solutions through which the colors are viewed, that may be passed over with only a word of reminder. Likewise we may refer to certain of the optical effects mentioned in Chapter VII and then pass on to the more serious difficulties in the application of the indicator method.

At the very beginning it will be well to emphasize the distinction which should be maintained between discrepancies attributable to the neglect of factors which may be evaluated by some general, if arbitrary, formulation and discrepancies attributable to the sum of what is ordinarily called "error" and specific phenomena beyond the range of any convenient formulation.

Up to this point in the development of the subject there has been used as the fundamental type-equation the following:

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a$$

For convenience of discussion consider separately the constant K_a, the ratio $\frac{[A^-]}{[HA]}$ and $[H^+]$.

In the derivation of the equation it was assumed that it is primarily the density of the number of particles in the solution-space that determines the equilibrium state. As the subject develops it will be found necessary to introduce appreciable corrections to this formula because it was deduced on assumptions far too ideal to meet the varying conditions of actual solutions. If we then insist on using the above formula, variation of condi-

tions will make it appear as if the so-called constant K_a were subject to appreciable variations. If under one set of conditions there is used a value of K_a standardized for another set of conditions an error will be introduced.

It is reasonable to assume as a close approximation that the ratio of the concentrations of two forms of the indicator will be determined by the "color" as described in Chapter III. However, see Halban and Ebert (1924). Their objection will now be neglected. Therefore, and in accordance with the theory of Chapter V, we use the ratio $\dfrac{[A^-]}{[HA]}$ as it stands uncorrected in the equation. On the other hand, we shall see, after having studied the theory of the hydrogen electrode, that there is no *exact* relation between the potential of a hydrogen cell and the hydrogen ion *concentrations*. However, there is an approximate relation.

Later there will be used the convenient equation

$$\frac{(H^+)\,(A^-)}{(HA)} = K_a \text{ or } \frac{[H^+]\,[A^-]}{[HA]} = K_a \frac{\gamma_{HA}}{\gamma_{H^+}\,\gamma_{A^-}}$$

Where () indicates "activity" and γ represents the "activity coefficient." Now it is doubtless a very close approach to $\dfrac{[A^-]}{[HA]}$ that is measured colorimetrically; it is (H^+), or $[H^+]\gamma_{H^+}$, and not $[H^+]$ that is measured electrometrically and ascribed to the buffer system; and it is $K_a \dfrac{\gamma_{HA}}{\gamma_{\overline{A}}}$ that is determined under one specific set of conditions and applied rather indiscriminately to all conditions.

The situation requires careful "unscrambling" which cannot well be done until the developments in subsequent chapters. In the meanwhile the interpretation of indicator conduct will be considered to be standardized by the use of standard comparison solutions having the pH values assigned in Chapter IX.

Because investigators have been content to proceed with this system of comparison and have not imposed upon themselves in all cases the accuracy demanded of the systematic type of study later to be indicated, most of the more directly applicable tables

of corrections are rather inaccurate.   They will be cited to indicate orders of magnitude found by the methods used.   The reader will do well to watch current literature for better systematized data which will probably be published extensively in the near future.

In the ordinary method of comparison, discrepancies have often been traced so clearly to two definite sources that they have been given categorical distinction.   They are the so-called "protein" and "salt" effects.

From what has already been said in previous pages, it will be seen that, if there are present in a tested solution bodies which remove the indicator or its ions from the field of action either by adsorption, or otherwise, the equilibria which have formed the basis of our treatment will be disturbed.   An indicator in such a solution may show a color intensity, or even a quality of color, which is different from that of the same concentration of the indicator in a solution of the same hydrogen ion concentration where no such disturbance occurs.   We could easily be led to attribute very different hydrogen ion concentrations to the two solutions. This situation is not uncommon when we are dealing with protein solutions, for in some instances there is distinctly evident the removal of the indicator from the field.   In other cases the discrepancy between electrometric and colorimetric measurements is not so clear, nor can it always be attributed solely to the indicator measurement.

"SALT EFFECTS"

If two solutions of inorganic material, each having the same pH-value, are tested with an indicator, we should expect the same color to appear.   If, however, these two solutions have different concentrations of salt, it may happen that the indicator colors are not the same.   As Sørensen (1909) and Sørensen and Palitzsch (1913) demonstrated, this effect of the salt content of a solution cannot be logically tested by adding the salt to one of two solutions which have previously been brought to the same pH-value. The added salt, no matter if it be a perfectly neutral salt, will change the pH-value of the solution.   Comparisons had best be made between solutions of the *same* pH-value.

So long as hydrogen electrode measurements are made the

standard, it is *convenient* to throw the burden of the "salt effect" upon the indicator; but neutral salts are known to displace electrode potential differences from the values estimated from the expected hydrogen ion *concentration.*

A standardization procedure may be illustrated as follows. The pH-value of the unknown is measured potentiometrically. Let it be 6.73. A portion of the same solution is now treated with the indicator and a color match is found with a standard buffer having an electrometrically determined pH-value of 6.70. The "error" is −0.03 pH unit and the correction necessary to bring the apparent colorimetric reading to the electrometric is +0.03.

Bjerrum (1914) gives an example of a case where the influence of the neutral salt is evidently upon the buffer equilibrium rather than on the indicator. An ammonium-ammonium salt buffer mixture and a borate buffer mixture are both made up to give the same color with phenolphthalein. On the addition of sodium chloride the color of phenolphthalein becomes stronger in the ammonium mixture and weaker in the borate mixture.

Let it be kept in mind that while neutral salts displace the electrode equilibrium and lead to different pH values of the standard, it is the measurement of the particular standard used that is usually taken as a standard of reference in the colorimetric comparison. The following illustrates a procedure with solutions of the same general nature. Sørensen and Palitzsch (1910) were studying the salt effects of indicators in sea water. They acidified the sea water and passed hydrogen through to displace carbon dioxid, and then neutralized it to the ranges of various indicators and buffer mixtures and compared colorimetric with electrometric measurements. In this way they found the following "errors."

INDICATOR	BUFFER	PARTS PER 1000 OF SALTS AND CORRESPONDING ERRORS			
		35	20	5	1
p-Nitrophenol............	Phosphate	+0.12	+0.08		
Neutral red..............	Phosphate	−0.10	−0.05	0	0
α-Naphthol phthalein...{	Borate	+0.22	+0.17	+0.03	−0 07
	Phosphate	+0.16	+0.11	−0.04	−0.14
Phenolphthalein..........	Borate	+0.21	+0.16	+0.05	−0.03

TABLE 27
Salt effect of indicators, after Kolthoff

INDICATOR	SALT	SALT CONCEN-TRATION	CORREC-TION	REMARKS
Tropaeolin OO (Orange IV).....	KCl	0.10 N	−0.05	Indicator suitable. NaCl has about same influence
	KCl	0.25 N	−0.01	
	KCl	0.50 N	+0.06	
	KCl	1.00 N	+0.23	
Methyl orange.....	KCl	0.10 N	−0.08	Indicator suitable. NaCl has about same influence
	KCl	0.25 N	−0.08	
	KCl	0.50 N	+0.02	
	KCl	1.00 N	+0.23	
Butter yellow.......	KCl	0.10 N	−0.08	Same errors as methyl orange but indicator flocculates with salt
Thymol blue (acid range)...........	KCl	0.10 N	−0.06	NaCl has same influence
	KCl	0.20 N	−0.06	
	KCl	0.50 N	−0.04	
	KCl	1.00 N	+0.05	
Brom phenol blue..	KCl	0.10 N	−0.05	Corrections large at weaker concentration of salt
	KCl	0.25 N	−0.15	
	KCl	0.50 N	−0.35	
	KCl	1.00 N	−0.35	
Brom cresol purple..	NaCl	0.50 N	−0.25	
Phenol red..........	NaCl	0.50 N	−0.15	At small concentrations of salt correction of opposite sign
Thymol blue........	NaCl	0.50 N	−0.17	
Methyl red..........	NaCl	0.50 N	+0.10	
p-Nitrophenol......:.	NaCl	0.50 N	−0.05	
Azo yellow 3G......	NaCl	0.50 N	0.00	
Phenolphthalein.....	NaCl	0.50 N	−0.17	
Nitramine..........	KCl	0.10 N	−0.06	NaCl has about same influence
	KCl	0.25 N	−0.12	
	KCl	0.50 N	−0.10	
	KCl	1.00 N	−0.29	

If, for example, sea water of about 3.5 per cent salt is matched against a standard borate solution with phenolphthalein and appears to be pH 8.43 the real value is pH 8.22. Compare table 44, page 213 and McClendon (1917).

TABLE 28

The salt error of cresol red at salinities from 5 to 35 parts of sea salts per 1000
(After Ramage and Miller)

Salinity	5	6	7	8	9	10	11	12
Correction	−0.11	−0.13	−0.14	−0.15	−0.16	−0.17	−0.18	−0.19
Salinity	13	14	15	16	17	18	19	20
Correction	−0.20	−0.21	−0.21	−0.22	−0.22	−0.23	−0.23	−0.24
Salinity	21	22	23	24	25	26	27	28
Correction	−0.24	−0.24	−0.25	−0.25	−0.25	−0.25	−0.26	−0.26
Salinity	29	30	31	32	33	34	35	
Correction	−0.26	−0.26	−0.26	−0.27	−0.27	−0.27	−0.27	

TABLE 29

Salt effects
(After Parsons and Douglas 1926)

INDICATOR	CORRECTION		
	1 molar	2 molar	3 molar
Thymol blue (alkaline range)	−0.22	−0.29	−0.34
Cresol red	−0.28	−0.32	−0.37
Phenol red	−0.21	−0.26	−0.29
Brom thymol blue	−0.19	−0.27	−0.29
Brom cresol purple	−0.26	−0.33	−0.31
Brom cresol green	−0.26	−0.31	−0.29
Brom phenol blue	−0.28	−0.37	−0.43
Thymol blue (acid range)	−0.10	−0.13	−0.12
Methyl red	−0.04	−0.01	+0.12

Such calibration is one of the very best ways to deal with the salt errors since it tends to bring measurements to a common experimental system of reference.

The following table taken from Prideaux (1917), illustrates the order of magnitude of the "salt error" in some instances.

INDICATOR	BUFFER USED	CHANGE OF pH IN PRESENCE OF 0.5 N NaCl
p-Benzene sulphonic acid azo naphthylamine....	Phosphate	−0.10
p-Nitrophenol..................................	Phosphate	+0.15
Alizarin sulphonic acid........................	Phosphate	+0.26
Neutral red....................................	Phosphate	−0.09
Rosolic acid...................................	Phosphate	+0.06
p-Benzene sulphonic acid azo α-naphthol.......	Phosphate	+0.12
Phenolphthalein................................	Phosphate	+0.12

Kolthoff (1922) gives table 27 page 181 showing the corrections to be applied for the "salt error" of various indicators. It should be noted that Kolthoff includes in this table data obtained when the hydrogen electrode potentials were taken as standard and also data in which the pH values were calculated. The two sets are not strictly comparable and therefore must be used with caution in theoretical work. We have eliminated from Kolthoff's table Congo red, Azolitmin, and Tropaeolin O (Chrysoïn) which Kolthoff describes as having salt errors so large that these indicators are useless.

Michaelis and his coworkers have determined the salt errors for a number of the nitrophenols, but, since the corrections are often intimately related to the constants used in Michaelis' method of operating, the reader is referred to the original literature for the details. See Chapter VI.

TABLE 30

Salt effect. New sulfonphthaleins

(After Cohen (1927))

[The values given below are corrections to be added to the colorimetric pH determinations to bring the values to the electrometric pH of the corresponding Clark and Lubs' buffers.]

MOLAR CONCENTRATION SALT	m-CRESOL PURPLE		BROM CRESOL GREEN	BROM PHENOL RED	CHLOR PHENOL RED	BROM CHLOR PHENOL BLUE
	Acid range	Alkaline range				
1.0	−0.14	−0.29	−0.32	−0.26	−0.26	−0.33
0.5	−0.09	−0.22	−0.26	−0.22	−0.20	−0.28
0.2	−0.02	−0.16	−0.16	−0.12	−0.10	−0.16
0.005	+0.11	+0.09	+0.09	+0.25	+0.23	+0.14

Ramage and Miller (1925) after a comparison of their own and Wells' (1920) data for cresol red give table 28 for use in the study of sea water.

Parsons and Douglas (1926) give a table (table 29) for "average" corrections which they suggest using in order to bring pH measurements of solutions of indicated concentrations of NaCl to conformity with the values of Clark and Lubs' standard buffers.

Cohen (1927) publishes table 30.
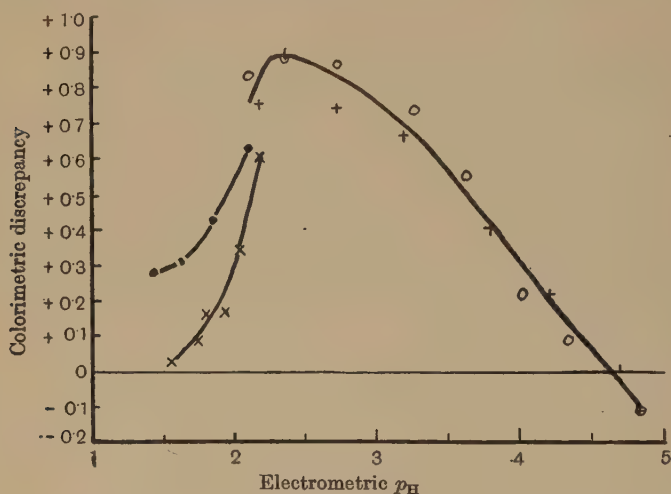
FIG. 32. VARIATION OF THE "PROTEIN ERROR," IN THE COLORIMETRIC DETERMINATION OF pH AS THE pH VALUE OF GELATINE SOLUTION CHANGES

$\bigcirc$ ≡ bromphenol blue and 1.0 per cent gelatine. $\bullet$ ≡ Thymol blue and 1.0 per cent gelatine. $+$ ≡ bromphenol blue and 0.4 per cent gelatine. $\times$ ≡ Thymol blue and 0.4 per cent gelatine. (After St. Johnston and Peard (1926).)

"PROTEIN" EFFECTS

The magnitude of "protein" effects may be roughly judged from the following tables.   The data, which could only be summarized in this way by neglecting some variation in the salt content of the solutions, include to some degree a salt effect.

Since it is not often that protein errors are presented in a systematic way, figure 32 by St. Johnston and Peard (1926) is

TABLE 31
"Protein" effects of indicators
(Data from Sørensen (1909))
Corrections to be added to apparent colorimetric reading to bring reading to the electrometric standard.

INDICATOR	CORRECTIONS	
	In 2% peptone 0.01 — 0.3 N salt	In 2% egg-white 0.07 — 0.3 N salt
Methyl violet..................................	−0.02	−0.19
Mauve...	−0.04	−0.19
Benzene-azo-diphenyl amine....................	−0.06	> −0.90
Tropaeolin OO................................	−0.27	> −1.40
Metanil yellow...............................	−0.30	> −1.40
Benzene-azo-benzylaniline.....................	+0.01	> −0.80
p-Benzene sulfonic acid-azo-benzylaniline......	−0.22	> −0.80
p-Benzene-sulfonic acid-azo-m-chlorodiethyl aniline.......................................	−0.41	
Töpfer's Indicator............................	−0.08	−0.53
Methyl orange................................	−0.18	
Benzene-azo-α-naphthylamine.................	−0.02	
p-Benzene sulfonic acid-azo-α-naphthylamine...	−0.03	+0.15
p-Nitrophenol................................	−0.06	−0.04
Neutral red...................................	+0.13	+0.68
Rosolic acid..................................	+0.08	+0.44
Tropaeolin OOO no. 1.........................	−0.12	+0.10
Phenolphthalein...............................	−0.01	+0.18
Thymolphthalein..............................	+0.01	+0.40
Alizarin yellow R.............................		+0.29
Tropaeolin O..................................		−0.30

TABLE 32
"Protein" effects of indicators
(Data from Clark and Lubs (1917))
Corrections are to be added to colorimetric readings to bring readings to electrometric standard.

INDICATOR	CORRECTIONS			
	Peptone-beef infusion	10% gelatine sol.	2% egg-white	Urine
Brom phenol blue.................	0.05			
Methyl red......................	−0.10		0.24	0.05
Brom cresol purple...............	0.01	0.04		0.01
Brom thymol blue................	0.10	0.04		0.02
Phenol red......................	0.04	0.20		0.00
Cresol red......................	0.03	0.20		
Thymol blue....................	0.04	0.20		
Cresolphthalein..................	−0.03	0.20		

TABLE 33

"Protein" effects of indicators

(Data of Cohen (1927))

[The values listed are the corrections to be added to colorimetric pH readings to bring them to the electrometric.]

INDICATOR	IN 5 PER CENT WITTE PEPTONE		CLARK AND LUBS[*]
	Series 1	Series 2	
m-Cresol purple (acid)..........................	−0.20	−0.20	
Thymol blue (acid)............................	−0.19	−0.20	
Brom phenol blue..............................	−0.28	−0.43	+0.05
Brom-chlor phenol blue.......................	−0.28	−0.43	
Brom cresol green............................	−0.10	−0.13	
Chlor phenol red.............................	+0.09	−0.07	
Brom phenol red..............................	+0.11	−0.10	
Brom cresol purple...........................	+0.11	−0.10	+0.01
Brom thymol blue.............................	+0.34	+0.07	+0.10
Phenol red...................................	+0.24	−0.01	+0.04
Cresol red...................................	+0.02	−0.03	+0.03
m-Cresol purple (alk.)........................	+0.03	−0.02	
Thymol blue (alk.)...........................	+0.09	−0.03	+0.04

[*] In a 1 per cent peptone-beef infusion broth.

TABLE 34

Protein errors with neutral red and with phenol red

(After Lepper and Martin (1927))

PSEUDO-GLOBULIN	NEUTRAL RED DEVIATION FROM ELECTROMETRIC pH	ALBUMIN	NEUTRAL RED DEVIATION FROM ELECTROMETRIC pH	PSEUDO-GLOBULIN	PHENOL RED DEVIATION FROM ELECTROMETRIC pH	ALBUMIN	PHENOL RED DEVIATION FROM ELECTROMETRIC pH
per cent		per cent		per cent		per cent	
0	0.00	0	0.00	0 (7.38)	0.00	0.00	0.00
0.17	0.00	0.23	0.00	2	0.00	0.03	0.00
0.33	0.00	0.047 (sic)	0.00	4	+0.02	0.06	−0.02
0.67	−0.05	0.095 (sic)	+0.10	8	+0.03	0.13	−0.03
1.35	−0.15	0.19	+0.20	12	+0.04		
2.70	−0.25	0.38	+0.30	0 (7.93)	0.00		
4.09	−0.45	0.75	+0.40	1.75	0.00		
5.40	−0.60	1.5	+0.51	3.5	+0.02		
8.17	−0.73	3.0	+0.58	7.0	+0.09		
10.80	−0.83			11.0	+0.12		
16.35	−0.85						

rather interesting. The apparent error is lowest near the iso-electric point of gelatin (4.7). Table 34 shows some cases in which the effect of the concentration of the protein is evident.

SYSTEMATIC TREATMENT

We owe to Brønsted (1921) the separation of the several different sorts of quantities appearing in the equation

$$\frac{[H^+][A^-]}{[HA]} = K_a \frac{\gamma_{HA}}{\gamma_{H^+}\,\gamma_{A^-}}$$

briefly mentioned earlier in this chapter. He applied certain of his equations for the estimation of the correction terms and obtained in some cases a rather striking agreement between observed salt-effects and calculated salt-effects. A more recent development will be mentioned in Chapter XXV (see page 511). There it will appear that salt effects are probably subject to much more systematic treatment than they have hitherto received. It will also appear that specific salt-effects remain. However, the first order corrections can be estimated by use of the Debye-Hückel equation described in Chapter XXV. Also the principle concerned can be put to good use. For instance, Hastings and Sendroy (1924) employ 0.154 M NaCl solution for the dilution of plasmas to be compared colorimetrically with phosphate standards. The ionic strength,[1] μ, of this sodium chloride solution is

$$1/2\ (0.154 \times 1^2 + 0.154 \times 1^2) = 0.154\mu$$

At 6.8 the ionic strength of the M/15 phosphate buffer is approximately

$$1/2\ (.0333 \times 2^2 + .0333 \times 1^2 + 0.1 \times 1^2) = 0.133\mu$$
$$\overline{H}PO_4 \qquad\qquad H_2\overline{P}O_4 \qquad\qquad Na^+$$

At 7.8 the ionic strength is about 0.190μ. Hence there is not a great difference between the ionic strengths of the diluted plasma and the buffer standard and consequently little difference in "salt error."

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[1] See pages 490 and 559.

It were much better to begin the systematization of salt-effects on such a basis than to continue longer with the pure empiricism which has characterized the data of the past. Unfortunately there are available as yet few systematic data and consequently the older tables are given in the foregoing pages. But see page 511 and figure 90.

It is not improbable that, even if the protein error cannot be precisely formulated with the aid of the Debye-Hückel equation, its description can be rationalized by the procedure suggested for the salt effects.

SPECIFIC ERRORS

The "protein" effect and the salt effect have been given prominence in the literature partly because both have to be taken into consideration in dealing with biological solutions, and partly because there is to be perceived underlying the salt error a most interesting phenomenon of rather general theoretical importance. However, this emphasis should not obscure the fact that there are specific conditions for each indicator which render that indicator useless for the determination of pH. For instance alizarin, in passing from the phosphate to the borate buffer mixtures, exhibits a sudden transition which has all the appearances of a specific effect of the borate upon the indicator. And alizarin is not alone in this peculiarity. This same alizarin in the presence of aluminium may form a lake and with proper pH control may be made a useful reagent for aluminium in place of a very poor acid-base indicator, cf. Williamson (1924). Zoller (1921) has called attention to the incompatibility between certain dyes and the phthalate buffers. Kolthoff (1926) notes an especially large error when methyl orange is used with phthalate buffer. Arndt and Nachtwey (1926) note errors with pyridine solutions and Michaelis (1926) states that sulfon phthaleins show errors with alkaloids that are not observed with nitrophenols.

Some indicators precipitate with certain cations, for instance Orange IV and Congo with alkali earths.

Sørensen (1909) paid particular attention to the extraction of an indicator from the aqueous phase by excess of chloroform etc. used as antiseptics.

Many indicators precipitate more or less slowly from standard

buffer solutions. When this is not noticed immediately it may lead to deceptions. Propyl red was rejected from Clark and Lubs' original list for this reason. Some indicators fade in light.[2]

Other indicators are reduced by suspensions of living cells. Some of these are useful as oxidation-reduction indicators; but the two classes should be so sharply distinguished that, when possible, the one property will not be used under conditions in which the other operates. In litmus-milk, for instance, the reduction and the acid-base change of the litmus may occur together and introduce complexity of interpretation as noted by Clark and Lubs (1917). They recommend that brom cresol purple be substituted for litmus in the acid test. Compare Reiss (1926). There should also be distinguished the reversible oxidation-reduction indicators and the irreversible. For a discussion of oxidation-reduction indicators see references found in Chapter XVIII and Appendix, tables K and L.

Some indicators, especially several of the triphenylmethane series, undergo some of their color changes slowly. Ignorance of this may lead to serious error.

Several common indicators, notably Congo, do not form true solutions and degree of dispersion contributes to the color. These indicators show abnormally large errors due partly to variations in degree of dispersion. They should not be expected to follow the ordinary equations except in a very approximate manner, if at all.

In short all possibilities must be watched lest the investigator venturing upon the study of some new solution, be misled by the mark of reliability placed upon an indicator tried under limited circumstances.

Wherever possible it is good practice to test doubtful cases with two indicators of widely different chemical composition.

TEMPERATURE EFFECTS

Let it be supposed that the simple equilibrium equation is applicable. A condition in its derivation was that the temperature should remain constant. If the indicator constant is deter-

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[2] Cullen (1922) reports that color standards may fade in the course of a week to the extent corresponding to about 0.02–0.04 pH unit.

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[2] Cullen (1922) reports that color standards may fade in the course of a week to the extent corresponding to about 0.02–0.04 pH unit.

CHAPTER IX

Standard Buffer Solutions for Colorimetric Comparison

*If arithmetic, mensuration and weighing be taken from any art,
that which remains will not be much.*—Plato.

The standard solutions used in the colorimetric method of determining hydrogen ion concentrations are buffer solutions with such well defined compositions that they can be accurately reproduced, and with pH values accurately defined by hydrogen electrode measurements. They generally consist of mixtures of some acid and its alkali salt. Several such mixtures have been carefully studied. An excellent set has been described by Sørensen (1912). This set may be supplemented by the acetic acid—sodium acetate mixtures most careful measurements of which have been made by Walpole (1914), and restudied by Cohn, Heyroth and Menkin (1928). The set may also be supplemented by Palitzsch's (1915) excellent boric acid-borax mixtures, or by one or another of the several series of mixtures which have been described in more recent years. A few of these will be mentioned but details will be given only for those mixtures which are, in the writer's limited knowledge, the more widely used.

In assigning values to these buffer solutions different authors have made somewhat different assumptions. See especially Chapter XXIII and those sections which deal with the hydrogen electrode.

clark and lubs' standards

Clark and Lubs (1916) have designed a set of standards which they believe are somewhat more conveniently prepared than are the Sørensen standards. Their set is composed of the following mixtures:

> Potassium chlorid + HCl
> Acid potassium phthalate + HCl
> Acid potassium phthalate + NaOH
> Acid potassium phosphate + NaOH
> Boric acid, KCl + NaOH

Clark and Lubs published their data for KCl-HCl mixtures as preliminary data. Although these data were retained in previous editions they have now been rejected and replaced by table 35a. The pH numbers in table 35a are calculated with the *assumption* that $\gamma_{H^+} = 0.84$ for these mixtures of constant ionic strength ($\mu = 0.1$). The assumption is not *entirely* justified; but, for convenience in the comparison of calculations, the third decimal of the pH numbers is given. The uncertainty affects the second decimal place.

In table 35 the compositions have been recalculated from the original data with the elimination of corrections made with the Bjerrum extrapolation. This should bring the numbers into conformity with the specifications of Chapter XXIII.

For a discussion of these mixtures, the methods used in determining their pH values, and the potential measurements we refer the reader to the original paper (*Journal of Biological Chemistry*, 1916, *25*, no. 3, p. 479). We may proceed at once to describe the details of preparation.

The various mixtures are made up from the following stock solutions: M/5 potassium chlorid (KCl), M/5 acid potassium phosphate (KH_2PO_4), M/5 acid potassium phthalate ($KHC_8H_4O_4$), M/5 boric acid with M/5 potassium chlorid (H_3BO_3, KCl), M/5 sodium hydroxid (NaOH), and M/5 hydrochloric acid (HCl). Although the subsequent mixtures are diluted to M/20 the above concentrations of the stock solutions are convenient for several reasons.

The water used in the crystallization of the salts and in the preparation of the stock solutions and mixtures should be redistilled. So-called "conductivity water," which is distilled first from acid chromate solution and again from barium hydroxid, is recommended, but it is not necessary.

M/5 potassium chlorid solution. (This solution will not be necessary except in the preparation of the most acid series of mixtures. See table.) The salt should be recrystallized three or four times and dried in an oven at about 120°C. for two days. The fifth molecular solution contains 14.912 grams in 1 liter.

M/5 acid potassium phthalate solution. Acid potassium phthalate may be prepared by the method of Dodge (1915–1920) modified as follows. Make up a concentrated potassium hydroxid solu-

tion by dissolving about 60 grams of a high-grade sample in about 400 cc. of water. To this add 50 grams of the commercial *resublimed* anhydrid of ortho phthalic acid.[1] Test a cool portion of the solution with phenol phthalein. If the solution is still alkaline, add more phthalic anhydrid; if acid, add more KOH. When roughly adjusted to a slight pink with phenol phthalein[2] add as much more phthalic anhydrid as the solution contains and heat till all is dissolved. Filter while hot, and allow the crystallization to take place slowly. The crystals should be drained with suction and recrystallized at least twice from distilled water.

Crystallization should not be allowed to take place below 20°C., for Dodge (1920) states:

A saturated solution of the acid phthalate on chilling will deposit crystals of a more acid salt, having the formula $2KHC_8H_4O_4 \cdot C_8H_6O_4$. These crystals are in the form of prismatic needles, easily distinguished under the microscope from the 6-sided orthorhombic plates of the salt $KHC_8H_4O_4$.

Dry the salt at 110°–115°C. to constant weight.

A fifth molecular solution contains 40.836 grams of the salt in 1 liter of the solution.

M/5 acid potassium phosphate solution.[3] A high-grade com-

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[1] While phthalic anhydride is now prepared commercially in very high purity and has become comparatively inexpensive, dealers will sometimes furnish material which is grossly impure. Among the more serious contaminants are benzoic acid, naphthols and possibly *quinones*. See Conover and Gibbs (1922). The best method of purification is that of sublimation in an apparatus of the type invented by Gibbs (1924). The better grades of phthalic anhydride are now made in remarkable purity by the vapor phase, catalytic oxidation of naphthalene; a process discovered by Gibbs (1918). Unless some purification is made when one has to use the lower grades of the anhydride, it may be necessary to recrystallize the potassium salt of the acid ten or more times before a sample is suitable for satisfactory hydrogen electrode measurements. A great deal of trouble is avoided by purchase of the highest grade anhydride in the first place.

[2] Use a diluted portion for the final test.

[3] The original measurements of Clark and Lubs were made with samples of phosphate which gave no clouding or flocs in their dilute solutions. Since then, and especially within recent years, the writer has had difficulty in obtaining phosphates, dilute solutions of which will not show this sign of impurity. No reasonable number of recrystallizations seem to rid the material of the contaminant. It appears to be an aluminium com-

mercial sample of the salt is recrystallized at least three times
from distilled water and dried to constant weight at 110–115°C.
A fifth molecular solution should contain 27.232 grams in 1 liter.
The solution should be distinctly red with methyl red and dis-
tinctly blue with brom phenol blue.

$M/5$ *boric acid* $M/5$ *potassium chlorid.*   Boric acid should be
recrystallized several times from distilled water.   It should be
air dried[4] in thin layers between filter paper and the constancy
of weight established by drying small samples in thin layers in a
desiccator over $CaCl_2$.   Purification of KCl has already been
noted.   It is added to the boric acid solution to bring the salt
concentration in the borate mixtures to a point comparable with
that of the phosphate mixtures so that colorimetric checks may
be obtained with the two series where they overlap.   One liter
of the solution should contain 12.4048 grams[5] of boric acid and
14.912 grams of potassium chlorid.

$M/5$ *sodium hydroxid solution.*   This solution is the most diffi-
cult to prepare, since it should be as free as possible from carbon-
ate.   A solution of sufficient purity for the present purposes may
be prepared from a high grade sample of the hydroxid in the
following manner.   Dissolve 100 grams NaOH in 100 cc. distilled
water in a Jena or Pyrex glass Erlenmeyer flask.   Cover the
mouth of the flask with tin foil and allow the solution to stand
over night till the carbonate has settled.   Then prepare a filter
as follows.   Cut a "hardened" filter paper to fit a Buchner funnel.
Treat it with warm, strong [1:1] NaOH solution.   After a few
minutes decant the sodium hydroxid and wash the paper first
with absolute alcohol, then with dilute alcohol, and finally with
large quantities of distilled water.   Place the paper on the Buch-
ner funnel and apply gentle suction until the greater part of the

pound.   A large sample of phosphoric acid which Dr. Ross prepared for
the writer by the method of Ross, Jones and Durgin (1925) was converted
to acid potassium phosphate.   This has been entirely satisfactory.

[4] Boric acid begins to lose "water of constitution" above 50°C.

[5] This weight was used on the assumption that the atomic weight of
boron is 11.0.   The atomic weight has since been revised and appears as
10.82 in the 1927 International Table of Atomic Weights.

Because the solutions were standardized with the above weight of boric
acid this weight should be used.

water has evaporated; but do not dry so that the paper curls.
Now pour the concentrated alkali upon the middle of the paper,
spread it with a glass rod making sure that the paper, under
gentle suction, adheres well to the funnel, and draw the solution
through with suction.   The clear filtrate is now diluted quickly,
after rough calculation, to a solution somewhat more concentrated
than N/1.   Withdraw 10 cc. of this dilution and standardize
roughly with an acid solution of known strength, or with a sample
of acid potassium phthalate.   From this approximate standardiza-
tion calculate the amount required to furnish an M/5 solution.
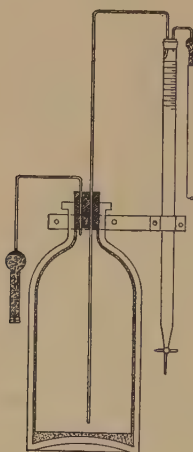
FIG. 33. PARAFFINED BOTTLE, WITH ATTACHED BURETTE AND SODA-LIME
TUBES FOR STANDARD ALKALI

Make the required dilution with the least possible exposure, and
pour the solution into a *paraffined*[6] bottle to which a calibrated 50
cc. buret and soda-lime guard tubes have been attached.   See
figure 33.   The solution should now be most carefully standard-
ized.   One of the simplest methods of doing this, and one which

[6] The author finds that thick coats of paraffin are more satisfactory than
the thin coats sometimes recommended.   Thoroughly clean and *dry* the
bottle, warm it and then pour in the melted paraffin.   Roll gently to make
an even coat and just before solidification occurs stand the bottle upright
to allow excess paraffin to drain to the bottom and there form a very sub-
stantial layer.

should always be used in this instance, is the method of Dodge (1915) in which use is made of the acid potassium phthalate purified as already described. Weigh out accurately on a chemical balance with standardized weights several portions of the salt of about 1.6 gram each. Dissolve in about 20 cc. distilled water and add 4 drops phenol phthalein. Pass a stream of CO_2-free air through the solution and titrate with the alkali till a faint but distinct pink is developed. It is preferable to use a factor with the solution rather than attempt adjustment to an exact M/5 solution.

If one should be fortunate enough to find that the concentrated sodium hydroxid solution had clarified itself without leaving suspended carbonate, the clear solution might be carefully pipetted from the sediment. Cornog (1921) describes another method as follows:

Distilled water contained in an Erlenmeyer flask is boiled to remove any carbon dioxide present, after which, when the water is cooled enough, ethyl ether is added to form a layer 3 or 4 cm. in depth. Pieces of metallic sodium, not exceeding about 1 cm. in diameter are then dropped into the flask. They will fall no further than the ether layer where they remain suspended. The water contained in the ether layer causes the slow formation of sodium hydroxid, which readily passes below to the water layer.

Cornog depends upon the evaporation of the ether as a barrier to CO_2. There are various ways in which the protection can be made more sure, and there are also various ways in which the aqueous solution may be separated from the ether.

From time to time there appear in the literature suggestions regarding the use of barium salts to remove the carbonate in alkali solutions.

In the author's opinion the next step to take, if the separation of carbonate from very concentrated NaOH solutions is not considered refined enough for the purpose at hand, is to proceed directly to the electrolytic preparation of an amalgam. Given a battery and two platinum electrodes this is a simple process. A *deep* layer of *redistilled* mercury is placed in a conical separatory funnel. The negative pole of the battery is led to this mercury by a glass-protected platinum wire. Over the mercury is placed a concentrated solution of recrystallized sodium chlorid and in this solution is dipped a platinum electrode connected

with the positive pole of the battery. The battery may have a potential of 4 to 6 volts. Electrolysis is continued with occasional *gentle* shaking to break up amalgam crystals forming on the mercury surface.

Boil the CO_2 out of a liter or so of redistilled water, and, while steam is still escaping, stopper the flask with a cork carrying a siphon, a soda-lime guard tube and a corked opening for the separatory funnel.

When the water is cool introduce the delivery tube of the separatory funnel and deliver the amalgam. Allow reaction to take place till a portion of the solution, when siphoned off to a buret and standardized, shows that enough hydroxid has been formed. Then siphon approximately the required amount into a boiled-out and protected portion of water. Mix thoroughly and standardize.

M/5 hydrochloric acid solution. Dilute a high grade hydro-chloric acid solution to about 20 per cent and distill. Dilute the distillate to approximately M/5 and standardize with the sodium hydroxid solution previously described. If convenient, it is well to standardize this solution carefully by the silver chlorid method and check with the standardized alkali. Standard solutions of hydrochloric acid are also prepared from constant boiling mixtures. See data and references by Foulk and Hollingsworth (1923).

The only solution which it is absolutely necessary to protect from the CO_2 of the atmosphere is the sodium hydroxid solution. Therefore all but this solution may be stored in ordinary bottles of resistant glass. The salt solutions, if adjusted to exactly M/5, may be measured from clean calibrated pipets.

These constitute the stock solutions from which the mixtures are prepared. The general relationships of these mixtures to their pH values are shown in figure 34. In this figure pH values are plotted as ordinates against X cc. of acid or alkali as abscissas. It will be found advantageous to plot this figure from table 35 with greatly enlarged scale so that it may be used as is Sørensen's chart (1909). The compositions of the mixtures at even intervals of 0.2 pH are given in table 35.

In any measurement the apportionment of scale divisions should accord with the precision. Scale divisions should not be
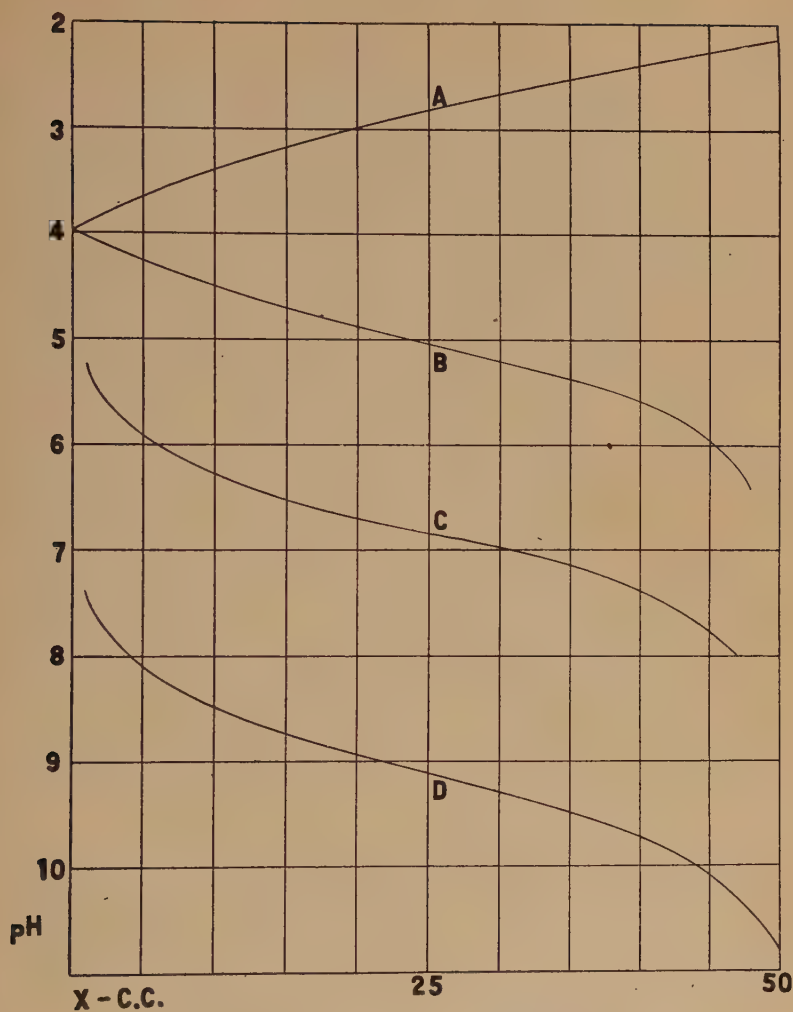
FIG. 34. CLARK AND LUBS' STANDARD MIXTURES

A. Fifty cubic centimeters 0.2 M KHPhthalate + X cc. 0.2 M HCl. Diluted to 200 cc.

B. Fifty cubic centimeters 0.2 M KHPhthalate + X cc. 0.2 M NaOH. Diluted to 200 cc.

C. Fifty cubic centimeters 0.2 M KH_2PO_4 + X cc. 0.2 M NaOH. Diluted to 200 cc.

D. Fifty cubic centimeters 0.2 M H_3BO_3, 0.2 M KCl + X cc. 0.2 M NaOH. Diluted to 200 cc.

TABLE 35

Composition of mixtures giving pH values at 20°C. at intervals of 0.2

Phthalate-HCl mixtures

2.2	50 cc. M/5 KHPhthalate	46.60 cc. M/5 HCl	Dilute to 200 cc.
2.4	50 cc. M/5 KHPhthalate	39.60 cc. M/5 HCl	Dilute to 200 cc.
2.6	50 cc. M/5 KHPhthalate	33.00 cc. M/5 HCl	Dilute to 200 cc.
2.8	50 cc. M/5 KHPhthalate	26.50 cc. M/5 HCl	Dilute to 200 cc.
3.0	50 cc. M/5 KHPhthalate	20.40 cc. M/5 HCl	Dilute to 200 cc.
3.2	50 cc. M/5 KHPhthalate	14.80 cc. M/5 HCl	Dilute to 200 cc.
3.4	50 cc. M/5 KHPhthalate	9.95 cc. M/5 HCl	Dilute to 200 cc.
3.6	50 cc. M/5 KHPhthalate	6.00 cc. M/5 HCl	Dilute to 200 cc.
3.8	50 cc. M/5 KHPhthalate	2.65 cc. M/5 HCl	Dilute to 200 cc.

Phthalate-NaOH mixtures

4.0	50 cc. M/5 KHPhthalate	0.40 cc. M/5 NaOH	Dilute to 200 cc.
4.2	50 cc. M/5 KHPhthalate	3.65 cc. M/5 NaOH	Dilute to 200 cc.
4.4	50 cc. M/5 KHPhthalate	7.35 cc. M/5 NaOH	Dilute to 200 cc.
4.6	50 cc. M/5 KHPhthalate	12.00 cc. M/5 NaOH	Dilute to 200 cc.
4.8	50 cc. M/5 KHPhthalate	17.50 cc. M/5 NaOH	Dilute to 200 cc.
5.0	50 cc. M/5 KHPhthalate	23.65 cc. M/5 NaOH	Dilute to 200 cc.
5.2	50 cc. M/5 KHPhthalate	29.75 cc. M/5 NaOH	Dilute to 200 cc.
5.4	50 cc. M/5 KHPhthalate	35.25 cc. M/5 NaOH	Dilute to 200 cc.
5.6	50 cc. M/5 KHPhthalate	39.70 cc. M/5 NaOH	Dilute to 200 cc.
5.8	50 cc. M/5 KHPhthalate	43.10 cc. M/5 NaOH	Dilute to 200 cc.
6.0	50 cc. M/5 KHPhthalate	45.40 cc. M/5 NaOH	Dilute to 200 cc.
6.2	50 cc. M/5 KHPhthalate	47.00 cc. M/5 NaOH	Dilute to 200 cc.

KH_2PO_4-NaOH mixtures

5.8	50 cc. M/5 KH_2PO_4	3.66 cc. M/5 NaOH	Dilute to 200 cc.
6.0	50 cc. M/5 KH_2PO_4	5.64 cc. M/5 NaOH	Dilute to 200 cc.
6.2	50 cc. M/5 KH_2PO_4	8.55 cc. M/5 NaOH	Dilute to 200 cc.
6.4	50 cc. M/5 KH_2PO_4	12.60 cc. M/5 NaOH	Dilute to 200 cc.
6.6	50 cc. M/5 KH_2PO_4	17.74 cc. M/5 NaOH	Dilute to 200 cc.
6.8	50 cc. M/5 KH_2PO_4	23.60 cc. M/5 NaOH	Dilute to 200 cc.
7.0	50 cc. M/5 KH_2PO_4	29.54 cc. M/5 NaOH	Dilute to 200 cc.
7.2	50 cc. M/5 KH_2PO_4	34.90 cc. M/5 NaOH	Dilute to 200 cc.
7.4	50 cc. M/5 KH_2PO_4	39.34 cc. M/5 NaOH	Dilute to 200 cc.
7.6	50 cc. M/5 KH_2PO_4	42.74 cc. M/5 NaOH	Dilute to 200 cc.
7.8	50 cc. M/5 KH_2PO_4	45.17 cc. M/5 NaOH	Dilute to 200 cc.
8.0	50 cc. M/5 KH_2PO_4	46.85 cc. M/5 NaOH	Dilute to 200 cc.

<div align="center">

TABLE 35—*Concluded*

Boric acid,   KCl-NaOH mixtures

</div>

 7.8 50 cc. M/5 H$_3$BO$_3$, M/5 KCl   2.65 cc. M/5 NaOH Dilute to 200 cc.
 8.0 50 cc. M/5 H$_3$BO$_3$, M/5 KCl   4.00 cc. M/5 NaOH Dilute to 200 cc.
 8.2 50 cc. M/5 H$_3$BO$_3$, M/5 KCl   5.90 cc. M/5 NaOH Dilute to 200 cc.
 8.4 50 cc. M/5 H$_3$BO$_3$, M/5 KCl   8.55 cc. M/5 NaOH Dilute to 200 cc.
 8.6 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 12.00 cc. M/5 NaOH Dilute to 200 cc.
 8.8 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 16.40 cc. M/5 NaOH Dilute to 200 cc.
 9.0 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 21.40 cc. M/5 NaOH Dilute to 200 cc.
 9.2 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 26.70 cc. M/5 NaOH Dilute to 200 cc.
 9.4 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 32.00 cc. M/5 NaOH Dilute to 200 cc.
 9.6 50 cc. M/5 H$_3$BO$_2$, M/5 KCl 36.85 cc. M/5 NaOH Dilute to 200 cc.
 9.8 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 40.80 cc. M/5 NaOH Dilute to 200 cc.
10.0 50 cc. M/5 H$_3$BO$_3$, M/5 KCl 43.90 cc. M/5 NaOH Dilute to 200 cc.

It is important to check the consistency of any particular set of these mixtures by comparing "5.8" and "6.2 phthalate" with "5.8" and "6.2 phosphate" using brom cresol purple. Also "7.8" and "8.0 phosphate" should be compared with the corresponding borates using cresol red.

<div align="center">

TABLE 35a

HCl-KCl Mixtures of Constant Ionic Strength, $\mu = 0.1$

Calculated on assumption that $\gamma_{H^+} = 0.84$

</div>

KCl MOLAR	HCl MOLAR	pH	COMPOSITION FOR 0.1 pH UNIT INCREMENT OF pH STOCK KCl: 0.2 MOLAR STOCK HCl: 0.2 MOLAR			
			KCl solution	HCl solution		pH
			cc.	*cc.*		
0.00	0.10	1.076[a]	0.00 +	59.5	dilute to 100 cc.	(1.0) ($\mu = 0.119$)
0.01	0.09	1.122	2.72 +	47.28	dilute to 100 cc.	1.1
0.02	0.08	1.173	12.45 +	37.55	dilute to 100 cc.	1.2
0.03	0.07	1.231	20.16 +	29.84	dilute to 100 cc.	1.3
0.04	0.06	1.298	26.30 +	23.70	dilute to 100 cc.	1.4
0.05	0.05	1.377	31.18 +	18.82	dilute to 100 cc.	1.5
0.06	0.04	1.474	35.03 +	14.95	dilute to 100 cc.	1.6
0.03	0.03	1.599	38.12 +	11.88	dilute to 100 cc.	1.7
0.01	0.02	1.774	40.57 +	9.43	dilute to 100 cc.	1.8
0.09	0.01	2.076[a]	42.51 +	7.49	dilute to 100 cc.	1.9
0.095	0.005	2.377	44.05 +	5.95	dilute to 100 cc.	2.0
0.098	0.002	2.775	45.27 +	4.73	dilute to 100 cc.	2.1
0.099	0.001	3.076	46.24 +	3.76	dilute to 100 cc.	2.2

[a] See page 472.

The original data for mixtures in table 35 were obtained with a saturated KCl calomel electrode as a working standard. This was compared with a group of tenth-normal KCl calomel half-cells. In calculating pH values for previous tables (see earlier editions and compare Clark and Lubs 1916, 1917) there were included Bjerrum extrapolations. These were especially large in the case of the HCl-KCl mixtures. The original data have now been used in recalculations in accord with the specifications of Chapter XXIII.

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so coarse that interpolations tax the judgment nor so fine as to be ridiculous. What scale divisions are best in the method under discussion it is difficult to decide, since the precision which may be attained depends somewhat upon the ability of the individual eye, and upon the material examined, as well as upon the means and the judgment used in overcoming certain difficulties which we shall mention later. Sørensen (1909) has arranged the standard solutions to differ by even parts of the components, a system which furnishes uneven increments in pH. Michaelis, (1910) on the other hand, makes his standards vary by about 0.3 pH so that the corresponding hydrogen ion concentrations are approximately doubled at each step. Certain general considerations lead to the conclusion that for most work estimation of pH values to the nearest 0.1 division is sufficiently precise, and that this precision can be obtained when the nature of the medium permits if the comparison standards differ by increments of 0.2 pH.

If smaller increments are desired it is permissible within limits to interpolate; but see table 43.

It is convenient to prepare 200 cc. of each of the mixtures and to preserve them in bottles each of which has its own 10 cc. pipet thrust through the stopper.[7] It takes but little more time to prepare 200 cc. than it does to prepare a 10 cc. portion, and if the larger volume is prepared there will not only be a sufficient quantity for a day's work but there will be some on hand for the occasional test.

Unless electrometric measurements can be used as control, we urge the most scrupulous care in the preparation and preservation of the standards. We have specified several recrystallizations of the salts used because commercial samples are not always to be relied upon.

[7] No serious error will be made if the tips of the pipettes be broken to permit rapid delivery.

SØRENSEN'S STANDARD BUFFER SOLUTIONS

Sørensen's standards are made as follows.   The stock solutions are:

1. A carefully prepared exact tenth normal solution of HCl.

2. A carbonate-free exact tenth normal solution of NaOH.

3. A tenth molecular glycocoll solution containing sodium chlorid, 7.505 grams glycocoll and 5.85 grams NaCl in 1 liter of solution.

4. An M/15 solution of primary potassium phosphate which contains 9.078 grams KH_2PO_4 in 1 liter of solution.

5. An M/15 solution of secondary sodium phosphate which contains 11.876 grams Na_2HPO_4, $2H_2O$ in 1 liter of solution.

6. A tenth molecular solution of secondary sodium citrate made from a solution containing 21.008 grams crystallized citric acid and 200 cc. carbonate-free N/1 NaOH diluted to 1 liter.

7. An alkaline borate solution made from 12.404 grams boric acid dissolved in 100 cc. carbonate-free N/1 NaOH and diluted to 1 liter.

The water shall be boiled, carbon dioxid-free, distilled water, and the solutions shall be protected against contamination by CO_2.

The materials for these solutions are described by Sørensen as follows.

Glycocoll (glycine)

Two grams glycocoll should give a clear solution in 20 cc. water and should test practically free of chlorid or sulfate.   Five grams should yield less than 2 mgm. of ash.   Five grams should yield, on distillation with 300 cc. of 5 per cent sodium hydroxid, less than 1 mgm. of nitrogen as ammonia.   The nitrogen content as determined by the Kjeldahl method should be 18.67 ± 0.1 per cent.

Primary phosphate, KH_2PO_4

The salt must dissolve clear in water and yield no test for chlorid or for sulfate.   When dried under 20 or 30 mm. pressure for a day at 100°C. the loss in weight should be less than 0.1 per cent, and on ignition the loss should be 13.23 ± 0.1 per cent. When compared colorimetrically with citrate mixtures the stock

phosphate solution should lie between "7" and "8 citrate-HCl." On addition of a drop of tenth-normal alkali or acid to 100 cc. the color of this phosphate solution with an indicator should be widely displaced.

Secondary phosphate Na_2HPO_4, $2 H_2O$

The salt with this content of water of crystallization is prepared by exposing to the ordinary atmosphere the crystals containing twelve moles of water.[8]   An exposure of about two weeks is generally sufficient.   The salt should yield a clear solution and yield no test for chlorid or sulfate.   A day of drying under 20 to 30 mm. pressure at 100°C. and then careful ignition to constant weight, should result in a 25.28 ± 0.1 per cent loss.   The stock solution should correspond on colorimetric test with "10 borate-HCl" and should be displaced beyond "8 borate-HCl" on addition of a drop of N/10 acid, and beyond "8 borate-NaOH" with a drop of alkali to 100 cc.

Citric acid, $C_6H_8O_7$, H_2O

The acid should dissolve clear in water, should yield no test for chlorid or sulfate and should give practically no ash.   The water of crystallization may be determined by drying under 20 to 30 mm. pressure at 70°C.   On drying in this manner the acid should remain colorless and lose 8.58 ± 0.1 per cent.   The acidity of the citric acid solution is determined by titration with 0.2 N barium hydroxid with phenolphthalein as indicator.   Titration is carried to a distinct red color of the indicator.

[8] There have been occasional complaints of the difficulty of preparing or keeping Sørensen's salt with a definite water content. See for example Clark and Lubs (1916) and Cohn (1927). Naegeli (1926) has brought together a number of references and a table of vapor pressures of the several hydrate systems which indicate that the subject is not yet in a satisfactory state. Naegeli prefers to make his buffer solutions with the heptahydrate, solutions of which are standardized gravimetrically. Sørensen states that he had no difficulty in obtaining the salt by exposure of the heptahydrate to the dry atmosphere of cold winter days. It should be noted that Sørensen took his usual care by determining the water content. This is advisable in variable climates.

Certain samples sold for the preparation of standard buffers and called "Sørensen's Phosphate" are wrongly labeled Na_2HPO_4.
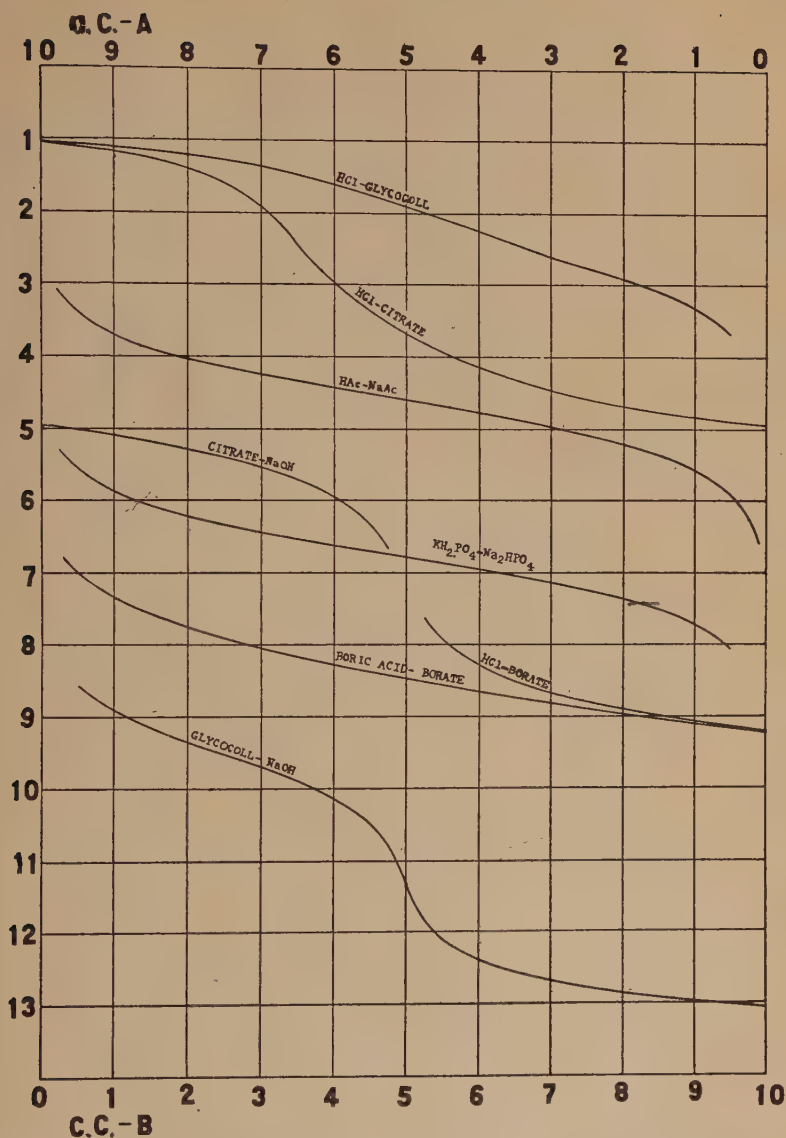
FIG. 35. Sørensen's Standard Mixtures, Walpole's Acetate Solutions and Palitzsch's Borate Solutions

Mixtures of A parts of acid constituent and B parts of basic constituent

TABLE 36

Sørensen's glycocoll-NaCl-NaOH mixtures

Walbum's values

Glycocoll: 7.505 grams Glycocoll + 5.85 grams NaCl per liter. NaOH: 0.1N.

VOLUME PARTS		pH AT INDICATED TEMPERATURE															
Glycocoll	NaOH	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°	32°	34°	37°	40°
9.5	0.5	8.75	8.70	8.66	8.62	8.58	8.53	8.49	8.45	8.40	8.37	8.32	8.28	8.24	8.18	8.12
9.0	1.0	9.10	9.06	9.02	8.97	8.93	8.88	8.84	8.79	8.75	8.71	8.67	8.62	8.58	8.52	8.45
8.0	2.0	9.54	9.50	9.45	9.40	9.36	9.31	9.26	9.22	9.17	9.13	9.08	9.04	9.00	8.92	8.85
7.0	3.0	9.90	9.85	9.80	9.75	9.71	9.66	9.61	9.56	9.51	9.46	9.42	9.37	9.32	9.25	9.18
6.0	4.0	10.34	10.29	10.24	10.18	10.14	10.09	10.03	9.98	9.93	9.88	9.83	9.78	9.73	9.66	9.58
5.5	4.5	10.68	10.63	10.58	10.53	10.48	10.42	10.37	10.32	10.27	10.22	10.17	10.12	10.07	9.99	9.91
5.1	4.9	11.29	11.24	11.18	11.12	11.07	11.01	10.96	10.90	10.85	10.79	10.74	10.68	10.62	10.54	10.46
5.0	5.0	11.53	11.48	11.42	11.36	11.31	11.25	11.20	11.14	11.09	11.03	10.97	10.92	10.86	10.78	10.70
4.9	5.1	11.80	11.74	11.68	11.62	11.57	11.51	11.45	11.39	11.33	11.27	11.22	11.16	11.10	11.02	10.93
4.5	5.5	12.34	12.28	12.22	12.16	12.10	12.04	11.98	11.92	11.86	11.80	11.74	11.68	11.62	11.53	11.44
4.0	6.0	12.65	12.59	12.52	12.46	12.40	12.33	12.27	12.21	12.15	12.09	12.03	11.96	11.90	11.81	11.72
3.0	7.0	12.92	12.86	12.80	12.73	12.67	12.60	12.54	12.48	12.42	12.35	12.29	12.23	12.17	12.07	11.98
2.0	8.0	13.12	13.06	12.99	12.92	12.86	12.79	12.73	12.66	12.60	12.53	12.47	12.41	12.34	12.25	12.15
1.0	9.0	13.23	13.16	13.09	13.03	12.97	12.90	12.83	12.77	12.70	12.64	12.57	12.51	12.45	12.35	12.25

70°	68°	66°	64°	62°	60°	58°	56°	54°	52°	50°	48°	46°	44°	42°		
7.48	7.52	7.56	7.61	7.65	7.69	7.74	7.78	7.82	7.86	7.91	7.95	7.99	8.03	8.07	0.5	9.5
7.79	7.84	7.88	7.93	7.97	8.02	8.06	8.10	8.14	8.19	8.24	8.28	8.32	8.37	8.41	1.0	9.0
8.16	8.21	8.26	8.30	8.35	8.40	8.44	8.49	8.53	8.58	8.63	8.67	8.72	8.76	8.81	2.0	8.0
8.45	8.50	8.55	8.60	8.65	8.70	8.74	8.79	8.84	8.89	8.94	8.99	9.03	9.08	9.13	3.0	7.0
8.82	8.88	8.93	8.98	9.03	9.08	9.13	9.18	9.23	9.28	9.33	9.38	9.43	9.48	9.53	4.0	6.0
9.15	9.20	9.25	9.30	9.35	9.41	9.46	9.51	9.56	9.61	9.66	9.71	9.76	9.81	9.86	4.5	5.5
9.62	9.68	9.74	9.79	9.85	9.90	9.96	10.02	10.07	10.13	10.18	10.24	10.29	10.35	10.40	4.9	5.1
9.87	9.93	9.98	10.04	10.09	10.14	10.20	10.26	10.32	10.37	10.43	10.48	10.54	10.59	10.64	5.0	5.0
10.05	10.11	10.17	10.23	10.29	10.35	10.40	10.46	10.52	10.58	10.64	10.69	10.75	10.81	10.87	5.1	4.9
10.54	10.60	10.66	10.72	10.78	10.84	10.90	10.96	11.02	11.08	11.14	11.20	11.26	11.32	11.38	5.5	4.5
10.78	10.84	10.91	10.97	11.03	11.10	11.16	11.22	11.28	11.34	11.41	11.47	11.53	11.59	11.65	6.0	4.0
11.03	11.09	11.16	11.22	11.28	11.35	11.41	11.47	11.54	11.60	11.66	11.73	11.79	11.85	11.91	7.0	3.0
11.18	11.25	11.31	11.38	11.44	11.51	11.57	11.64	11.70	11.77	11.83	11.89	11.96	12.02	12.08	8.0	2.0
11.28	11.35	11.41	11.48	11.54	11.61	11.67	11.74	11.80	11.87	11.94	12.00	12.06	12.13	12.19	9.0	1.0

TABLE 37

Sørensen's borate—NaOH mixtures

(Walbum's values)

Borate: 12.404g H_3BO_3 + 100 cc. N NaOH per l.
NaOH: 0.1 N

Temperature	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°	32°	34°	37°	40°
10 Borate	9.30		9.27		9.24		9.21		9.18		9.15		9.13	9.11	9.08
9 Borate + 1 NaOH	9.42		9.39		9.36		9.33		9.29		9.26		9.23	9.20	9.18
8 Borate + 2 NaOH	9.57		9.54		9.50		9.46		9.43		9.39		9.35	9.32	9.30
7 Borate + 3 NaOH	9.76		9.72		9.68		9.63		9.59		9.55		9.50	9.47	9.44
6 Borate + 4 NaOH	10.06	10.04	10.02	9.99	9.97	9.94	9.91	9.88	9.86	9.83	9.80	9.78	9.75	9.71	9.67
5 Borate + 5 NaOH	11.24	11.20	11.16	11.12	11.08	11.04	10.99	10.95	10.91	10.86	10.82	10.78	10.74	10.68	10.61
4 Borate + 6 NaOH	12.64	12.58	12.51	12.45	12.38	12.32	12.25	12.19	12.13	12.06	12.00	11.93	11.87	11.77	11.68

Temperature	42°	44°	46°	48°	50°	52°	54°	56°	58°	60°	62°	64°	66°	68°	70°
10 Borate		9.05		9.02		9.00		8.97		8.93		8.90			8.86
9 Borate + 1 NaOH		9.15		9.11		9.08		9.05		9.01		8.98			8.94
8 Borate + 2 NaOH		9.26		9.22		9.18		9.15		9.11		9.08			9.02
7 Borate + 3 NaOH		9.40		9.35		9.31		9.27		9.22		9.18			9.12
6 Borate + 4 NaOH	9.64	9.62	9.59	9.56	9.54	9.51	9.48	9.46	9.43	9.40	9.38	9.35	9.33	9.30	9.28
5 Borate + 5 NaOH	10.57	10.53	10.49	10.44	10.40	10.36	10.32	10.27	10.23	10.19	10.13	10.10	10.06	10.02	9.98
4 Borate + 6 NaOH	11.61	11.55	11.48	11.42	11.36	11.29	11.23	11.17	11.10	11.04	10.98	10.91	10.85	10.78	10.72

TABLE 38
Sørensen's borate—HCl mixtures
(Walbum's values)
Borate: 12.404g H_3BO_3 + 100 cc. N NaOH per l.
    HCl: 0.1 N

Temperature......................	10°	20°	30°	40°	50°	60°	70°
10.0 Borate................	9.30	9.23	9.15	9.08	9.00	8.93	8.86
9.5 Borate + 0.5 HCl.....	9.22	9.15	9.08	9.01	8.94	8.87	8.80
9.0 Borate + 1.0 HCl.....	9.14	9.07	9.01	8.94	8.87	8.80	8.74
8.5 Borate + 1.5 HCl.....	9.06	8.99	8.92	8.86	8.80	8.73	8.67
8.0 Borate + 2.0 HCl.....	8.96	8.89	8.83	8.77	8.71	8.65	8.59
7.5 Borate + 2.5 HCl.....	8.84	8.79	8.72	8.67	8.61	8.55	8.50
7.0 Borate + 3.0 HCl.....	8.72	8.67	8.61	8.56	8.50	8.45	8.40
6.5 Borate + 3.5 HCl.....	8.54	8.49	8.44	8.40	8.35	8.30	8.26
6.0 Borate + 4.0 HCl.....	8.32	8.27	8.23	8.19	8.15	8.11	8.08
5.75 Borate + 4.25 HCl...	8.17	8.13	8.09	8.06	8.02	7.98	7.95
5.5 Borate + 4.5 HCl.....	7.96	7.93	7.89	7.86	7.82	7.79	7.76
5.25 Borate + 4.75 HCl...	7.64	7.61	7.58	7.55	7.52	7.49	7.47

TABLE 39
Sørensen's citrate—HCl mixtures
Citrate: 21.008g Crystn. Citric Acid + 200 cc. N NaOH per l.
HCl: 0.1 N

Temperature 18°C.

CITRATE	HCl	pH
cc.	cc.	
0.0	10.0	1.038*
1.0	9.0	1.173
2.0	8.0	1.418
3.0	7.0	1.925
3.33	6.67	2.274
4.0	6.0	2.972
4.5	5.5	3.364
4.75	5.25	3.529
5.0	5.0	3.692
5.5	4.5	3.948
6.0	4.0	4.158
7.0	3.0	4.447
8.0	2.0	4.652
9.0	1.0	4.830
9.5	0.5	4.887
10.0	0.0	4.958

* Note inconsistency with table 35a.

TABLE 40

Sørensen's glycocoll—HCl mixtures
Glycocoll: 0.1 M Glycocoll + 0.1 M NaCl per l.
HCl: 0.1 N

Temperature 18°C.

GLYCOCOLL	HCl	pH
cc.	cc.	
0.0	10.0	1.038*
1.0	9.0	1.146
2.0	8.0	1.251
3.0	7.0	1.419
4.0	6.0	1.645
5.0	5.0	1.932
6.0	4.0	2.279
7.0	3.0	2.607
8.0	2.0	2.922
9.0	1.0	3.341
9.5	0.5	3.679

Note inconsistency with table 35a.

TABLE 41

Sørensen's phosphate mixtures
Secondary: 11.876g Na$_2$ HPO$_4$ · 2 H$_2$O per l.
Primary: 9.078g KH$_2$PO$_4$ per l.

Temperature 18°C.

SECONDARY	PRIMARY	pH
cc.	cc.	
0.25	9.75	5.288
0.5	9.5	5.589
1.0	9.0	5.906
2.0	8.0	6.239
3.0	7.0	6.468
4.0	6.0	6.643
5.0	5.0	6.813
6.0	4.0	6.979
7.0	3.0	7.168
8.0	2.0	7.381
9.0	1.0	7.731
9.5	0.5	8.043

Boric acid, H_3BO_3

Twenty grams of boric acid should go completely into solution in 100 cc. of water when warmed on a strongly boiling water bath. This solution is cooled in ice water and the filtrate from the crystallized boric acid is tested as follows. It should give no tests for chlorides or sulfates. It should be orange to methyl orange. A drop of N/10 HCl added to 5 cc. should make the filtrate red to methyl orange. Twenty cubic centimeters of the filtrate evaporated in platinum, treated with about 10 grams of hydrofluoric acid and 5 cc. of concentrated sulfuric acid and reëvaporated, ignited and weighed, should yield less than 2 mgm. when corrected for non-volatile matter in the HF.

Tables 36–42 give the Sørensen mixtures with the corresponding pH values. Mixtures whose pH values are considered by Sørensen to be too uncertain and which he has indicated by brackets are omitted from these tables. The third decimal of Sørensen's tables are given by Sørensen in small type.

TABLE 42

Sørensen's citrate—NaOH mixtures

(Walbum's values)

Citrate: 21.008g Crystn. Citric Acid + 200 cc. N NaOH per l.
NaOH: 0.1 N

Temperature	10°	20°	30°	40°	50°	60°	70°
10.0 Citrate	4.93	4.96	5.00	5.04	5.07	5.10	5.14
9.5 Citrate + 0.5 NaOH	4.99	5.02	5.06	5.10	5.13	5.16	5.20
9.0 Citrate + 1.0 NaOH	5.08	5.11	5.15	5.19	5.22	5.25	5.29
8.0 Citrate + 2.0 NaOH	5.27	5.31	5.35	5.39	5.42	5.45	5.49
7.0 Citrate + 3.0 NaOH	5.53	5.57	5.60	5.64	5.67	5.71	5.75
6.0 Citrate + 4.0 NaOH	5.94	5.98	6.01	6.04	6.08	6.12	6.15
5.5 Citrate + 4.5 NaOH	6.30	6.34	6.37	6.41	6.44	6.47	6.51
5.25 Citrate + 4.75 NaOH	6.65	6.69	6.72	6.76	6.79	6.83	6.86

WALBUM'S DATA

Walbum (1920) has determined the pH values for the Sørensen mixtures at temperatures of 10°, 18°, 28°, 37°, 46°, 62° and 70°C. and has interpolated data for intervening temperatures. He finds that the alteration of pH with temperature is for the most part negligible for the phosphate mixtures, the glycocoll-HCl mixtures and the citrate-HCl mixtures. In his tables will be found Sørensen's values at 18°. Tables 39, 40 and 41 are taken from Sørensen's paper of 1912.

Sørensen and Walbum used the Bjerrum extrapolation which results in making the pH numbers of the more acid solutions less than they would be had the specifications of Chapter XXIII been used.

HASTINGS AND SENDROY'S DATA

For the special purposes of urine and blood analysis Hastings and Sendroy (1924) required smaller increments of pH than are usually provided in tables of buffer systems. They also desired standardized values at 20° and 38°. Table 43 contains their data.

TABLE 43

M/15 phosphate mixtures at 20° and 38°

(Hastings and Sendroy (1924))

0.1 N HCl : pH 1.08 used as standard of reference

M/15 Na₂HPO₄	M/15 KH₂PO₄	pH DETERMINED AT 20°	pH DETERMINED AT 38°
cc.	cc.		
49.6	50.4	6.809	6.781
52.5	47.5	6.862	6.829
55.4	44.6	6.909	6.885
58.2	41.8	6.958	6.924
61.1	38.9	7.005	6.979
63.9	36.1	7.057	7.028
66.6	33.4	7.103	7.076
69.2	30.8	7.154	7.128
72.0	28.0	7.212	7.181
74.4	25.6	7.261	7.230
76.8	23.2	7.313	7.288
78.9	21.1	7.364	7.338
80.8	19.2	7.412	7.384
82.5	17.5	7.462	7.439
84.1	15.9	7.504	7.481
85.7	14.3	7.561	7.530
87.0	13.0	7.610	7.576
88.2	11.8	7.655	7.626
89.4	10.6	7.705	7.672
90.5	9.5	7.754	7.726
91.5	8.5	7.806	7.776
92.3	7.7	7.848	7.825
93.2	6.8	7.909	7.877
93.8	6.2	7.948	7.919
94.7	5.3	8.018	7.977

PALITZSCH'S STANDARD BUFFER SOLUTIONS

Palitzsch (1922) designed his standards for the special convenience of those investigators whose interests center upon the determination of the pH values of sea waters.

TABLE 44

pH values of borax-borate mixtures at 18°C. and "salt-effects" for phenol-phthalein and α-naphtholphthalein

(Palitzsch (1922))

Borax solution: 19.108 grams $Na_2B_4O_7.10H_2O$ in 1 l.   Boric acid solution: 12.404 grams H_3BO_3 + 2.925 grams NaCl in 1 l.

STANDARD SOLUTIONS			TRUE pH VALUES OF SEA WATER CONTAINING S PARTS PER 1000 SALINITY AT COLOR-MATCH WITH STANDARD											
Borax	Boric acid	pH	S = 36	S = 30	S = 26	S = 22	S = 18	S = 14	S = 10	S = 6	S = 4	S = 2	S = 1	
cc.	cc.													
6.0	4.0	8.69	8.48	8.49	8.50	8.52	8.54	8.57	8.59	8.63	8.66	8.69	8.72	Phenol-phthalein
5.5	4.5	8.60	8.39	8.40	8.41	8.43	8.45	8.48	8.50	8.54	8.57	8.60	8.63	
5.0	5.0	8.51	8.30	8.31	8.32	8.34	8.36	8.39	8.41	8.45	8.48	8.51	8.54	
4.5	5.5	8.41	8.20	8.21	8.22	8.24	8.26	8.29	8.31	8.35	8.38	8.41	8.44	
4.0	6.0	8.31	8.10	8.11	8.12	8.14	8.16	8.19	8.21	8.25	8.28	8.31	8.34	
3.5	6.5	8.20	7.99	8.00	8.01	8.03	8.05	8.08	8.10	8.14	8.17	8.20	8.23	
4.5	5.5	8.41	8.19	8.20	8.21	8.23	8.25	8.28	8.32	8.37	8.40	8.45	8.48	α-Naphtholphthalein
4.0	6.0	8.31	8.09	8.10	8.11	8.13	8.15	8.18	8.22	8.27	8.30	8.35	8.38	
3.5	6.5	8.20	7.98	7.99	8.00	8.02	8.04	8.07	8.11	8.16	8.19	8.24	8.27	
3.0	7.0	8.08	7.86	7.87	7.88	7.90	7.92	7.95	7.99	8.04	8.07	8.12	8.15	
2.5	7.5	7.94	7.72	7.73	7.74	7.76	7.78	7.81	7.85	7.90	7.93	7.98	8.01	
2.3	7.7	7.88	7.66	7.67	7.68	7.70	7.72	7.75	7.79	7.84	7.87	7.92	7.95	
2.0	8.0	7.78	7.56	7.57	7.58	7.60	7.62	7.65	7.69	7.74	7.77	7.82	7.85	
1.5	8.5	7.60	7.38	7.39	7.40	7.42	7.44	7.47	7.51	7.56	7.59	7.64	7.67	
1.0	9.0	7.36	7.14	7.15	7.16	7.18	7.20	7.23	7.27	7.32	7.35	7.40	7.43	
0.6	9.4	7.09	6.87	6.88	6.89	6.91	6.93	6.96	7.00	7.05	7.08	7.13	7.16	
0.3	9.7	6.77	6.55	6.56	6.57	6.59	6.61	6.64	6.68	6.73	6.76	6.81	6.84	

The stock solutions are: an M/20 Borax solution containing 19.108 grams[9] $Na_2B_4O_7$ 10 H_2O in 1 liter; and an M/5 Boric acid, NaCl solution containing 12.404 grams[9] H_3BO_3 and 2.925 grams NaCl in 1 liter.

[9] The values given by Palitzsch were calculated upon the basis of 11.0 as the atomic weight of boron. Since this was the value used, the new value of 10.82 given in the atomic weight table of International Critical

Since the buffer solutions are used more frequently for the study of sea water, table 44 includes the values of the salt effects of sea water on two indicators.   For salt effects in general see Chapters VIII and XXV.

McILVAINE'S STANDARD BUFFER SOLUTIONS

McIlvaine (1921) employs a mixture of 0.2 M disodium phosphate and 0.1 M citric acid.   The citrate system functions as a buffer in the region of pH between that buffered by the phosphoric

TABLE 45

McIlvaine's standards

pH	0.2 M Na₂HPO₄	0.1 M CITRIC ACID	pH	0.2 M Na₂HPO₄	0.1 M CITRIC ACID
	cc.	cc.		cc.	cc.
2.2	0.40	19.60	5.2	10.72	9.28
2.4	1.24	18.76	5.4	11.15	8.85
2.6	2.18	17.82	5.6	11.60	8.40
2.8	3.17	16.83	5.8	12.09	7.91
3.0	4.11	15.89	6.0	12.63	7.37
3.2	4.94	15.06	6.2	13.22	6.78
3.4	5.70	14.30	6.4	13.85	6.15
3.6	6.44	13.56	6.6	14.55	5.45
3.8	7.10	12.90	6.8	15.45	4.55
4.0	7.71	12.29	7.0	16.47	3.53
4.2	8.28	11.72	7.2	17.39	2.61
4.4	8.82	11.18	7.4	18.17	1.83
4.6	9.35	10.65	7.6	18.73	1.27
4.8	9.86	10.14	7.8	19.15	0.85
5.0	10.30	9.70	8.0	19.45	0.55

acid-mono phosphate system and that buffered by the mono phosphate-diphosphate system.   Consequently the range pH 2.2–pH 8.0 is covered by mixtures of but two stock solutions.   If samples of the salt and acid are well characterized this combination is convenient for many purposes.

McIlvaine's data are summarized in table 45.

Tables should not be used in calculating the composition of the *specific* solutions given by Palitzsch.

OTHER STANDARD BUFFER SOLUTIONS

Walpole's (1914) data on acetate solutions were included in the reconsideration of acetate solutions by Cohn, Heyroth and Menkin (1928). Their data are shown in tables 49A and 49B.

Atkins and Pantin (1926) have described some buffer solutions composed of boric acid, potassium chloride and sodium carbonate. Range: 7.44–11.0.

Prideaux and Ward (1924) propose a buffer mixture in which is found phenyl acetic acid (pK = "4.27"), phosphoric acid

TABLE 46

Alkaline soda-borax buffer solutions of Kolthoff and Vlesschhouwer (1927) at 18°

See page 477 for note on standard of reference. Solution A: 5.30 grams Na_2CO_3 per liter. Solution B: 19.10 grams $Na_2B_4O_7 \cdot 10 H_2O$ per liter.

MIXTURE		pH
Cubic centimeter A	Cubic centimeter B	
0	100	9.2
35.7	64.3	9.4
55.5	44.5	9.6
66.7	33.3	9.8
75.4	24.6	10.0
82.15	17.85	10.2
86.9	13.1	10.4
91.5	8.5	10.6
94.75	5.25	10.8
97.3	2.7	11.0

(pK values: "1.96, 6.85, 11.52") and boric acid (pK = "9.22"). The object of this combination is to provide a "universal buffer" (cf. table 45). Acree and his coworkers have worked on the same idea. The principles concerned in overlapping the buffer effects of different systems are discussed in systematic form by Van Slyke (1922).

Kolthoff and Vleeschhouwer (1926) have published data on mixtures of mono potassium citrate with HCl, NaOH, and with citric acid and borax. See corrections by Kolthoff and Vleeschhouwer (1927).

Kolthoff (1925) has described buffer mixtures of succinic acid and borax and of acid potassium phosphate and borax.

Avery, Mellon and Acree (1921) describe buffer mixtures the salts of which are put up in tablet form. If properly prepared and preserved these might be especially useful for field work and for the occasional rough measurement.

The following tables of Kolthoff and Vleeschhouwer (1927) give pH values for alkaline regions of pH. The standard of calculation was

$$\text{pH} = 2.038 \text{ for } 0.01 \text{ N HCl} + 0.09 \text{ N KCl at } 18°.$$

TABLE 47

Alkaline phosphate buffer solutions of Kolthoff and Vleeschhouwer (1927) at 18°

See page 477 for note on standard of reference. Solution A: 17.81 grams $Na_2HPO_4 \cdot 2 H_2O$ per liter. Solution B: 0.1 N NaOH.

MIXTURE	pH
25 cc. A + 4.13 cc. B, dilute to 50 cc.	11.00
25 cc. A + 6.00 cc. B, dilute to 50 cc.	11.20
25 cc. A + 8.67 cc. B, dilute to 50 cc.	11.40
25 cc. A + 12.25 cc. B, dilute to 50 cc.	11.60
25 cc. A + 16.65 cc. B, dilute to 50 cc.	11.80
25 cc. A + 21.60 cc. B, dilute to 50 cc.	12.00

COHN'S SYSTEM OF BUFFER STANDARDS

An excellent innovation in the construction of buffer standards has been introduced by Cohn (1927) and Cohn, Heyroth and Menkin (1928).

As ordinarily prepared, buffer solutions vary appreciably in ionic strength. The ionic strength is determined by multiplying the concentration of each ion by the square of that ion's valence number, summing all such products and dividing by two. See page 490. As a consequence of the variation in ionic strength the corrections to a common basis of reference, which may be calculated by the Debye-Hückel equation, vary. (The Debye-

Hückel equation is discussed in Chapter XXV.) Furthermore there are occasions to employ buffers of different known ionic strength.

TABLE 48A

pK' values of phosphate system

(After Cohn (1927))

Temperature 18°C.

TOTAL PHOS- PHATE	MOLE FRACTION OF TOTAL PHOSPHATE AS K_2HPO_4								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
M									
0.1	6.788	6.781	6.774	6.769	6.765	6.760	6.755	6.753	6.752
0.2	6.676	6.679	6.679	6.682	6.685	6.687	6.688	6.692	6.698
0.3	6.596	6.608	6.616	6.631	6.640	6.651	6.658	6.668	6.682
0.4	6.530	6.553	6.570	6.593	6.611	6.628	6.642	6.659	6.681
0.5	6.472	6.505	6.531	6.564	6.590	6.615	6.634	6.659	6.688
0.6	6.420	6.463	6.498	6.540	6.574	6.606	6.632	6.664	6.702
0.8	6.325	6.390	6.441	6.503	6.553	6.600	6.639	6.684	6.737
1.0	6.238	6.324	6.393	6.474	6.540	6.602	6.653	6.712	6.781
1.2	6.157	6.265	6.351	6.450	6.533	6.609	6.672	6.746	6.830

Cohn finds that the pH values of phosphate buffer solutions may be calculated by means of the formula.

$$pH = pK + \log \frac{[HPO_4^{--}]}{[H_2PO_4^{-}]} + \log \frac{\gamma_2}{\gamma_1}$$

In place of $pK + \log \frac{\gamma_2}{\gamma_1}$ may be substituted pK', the values of which are found in tables 48A and 48B.

For example: a mixture making 0.1 M KH_2PO_4 and 0.3 M K_2HPO_4 would be 0.4 M with respect to total phosphate and the mole fraction of total phosphate as K_2HPO_4 would be $\frac{0.3}{0.4} = 0.75$. Interpolation in table 48A shows pK' = 6.651.

$$pH = 6.651 + \log \frac{0.3}{0.1} = 7.128$$

TABLE 48B

pK' values of phosphate system

(After Cohn (1927))

Temperature 18°C.

IONIC STRENGTH OF PHOS- PHATE SOLUTION	MOLE FRACTION OF TOTAL PHOSPHATE AS K_2HPO_4								
μ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.1	6.813	6.824	6.831	6.837	6.841	6.844	6.846	6.848	6.850
0.2	6.709	6.731	6.745	6.757	6.765	6.771	6.775	6.779	6.783
0.3	6.634	6.667	6.688	6.706	6.718	6.727	6.733	6.739	6.745
0.4	6.573	6.617	6.645	6.669	6.685	6.697	6.705	6.713	6.721
0.5	6.520	6.575	6.610	6.640	6.660	6.675	6.685	6.695	6.705
0.6	6.472	6.538	6.580	6.616	6.640	6.658	6.670	6.682	6.694
0.7	6.428	6.505	6.554	6.596	6.624	6.645	6.659	6.673	6.687
0.8	6.387	6.475	6.531	6.579	6.611	6.635	6.651	6.667	6.683
0.9	6.348	6.447	6.510	6.564	6.600	6.627	6.645	6.663	6.681
1.0	6.310	6.420	6.490	6.550	6.590	6.620	6.640	6.660	6.680
1.1	6.274	6.395	6.472	6.538	6.582	6.615	6.637	6.659	6.681
1.2	6.238	6.370	6.454	6.526	6.574	6.610	6.634	6.658	6.682
1.3	6.204	6.347	6.438	6.516	6.568	6.607	6.633	6.659	6.685
1.4	6.170	6.324	6.422	6.506	6.562	6.604	6.632	6.660	6.688
1.5	6.137	6.302	6.407	6.497	6.557	6.602	6.632	6.662	6.692
1.6		6.281	6.393	6.489	6.553	6.601	6.633	6.665	6.697
1.7		6.260	6.379	6.481	6.549	6.600	6.634	6.668	6.702
1.8			6.366	6.474	6.546	6.600	6.636	6.672	6.708
1.9			6.353	6.467	6.543	6.600	6.638	6.676	6.714
2.0				6.460	6.540	6.600	6.640	6.680	6.720
2.1				6.454	6.538	6.601	6.643	6.685	6.727
2.2				6.448	6.536	6.602	6.646	6.690	6.734
2.3					6.534	6.603	6.649	6.695	6.741
2.4					6.533	6.605	6.653	6.701	6.749
2.5						6.607	6.657	6.707	6.757
2.6						6.608	6.660	6.712	6.764
2.7						6.611	6.665	6.719	6.773
2.8							6.669	6.725	6.781
2.9							6.673	6.731	6.789
3.0								6.738	6.798

Interpolated values of $-\log \gamma$ for mixtures of acetic acid and sodium acetate
(After Cohn, Heyroth and Menkin (1928))
Temperature 18°C.

CONCEN-TRATION OF TOTAL ACETATE	MOLE FRACTION OF TOTAL ACETATE AS CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\log \gamma$								
μ									
0.05	0.034	0.045	0.053	0.060	0.064	0.069	0.071	0.075	0.073
0.10	0.047	0.062	0.071	0.078	0.084	0.088	0.091	0.093	0.089
0.20	0.065	0.082	0.092	0.099	0.105	0.108	0.109	0.109	0.101
0.40	0.088	0.106	0.115	0.119	0.123	0.123	0.120	0.118	0.100
0.60	0.105	0.120	0.127	0.130	0.129	0.125	0.119	0.112	0.089
0.80	0.118	0.130	0.136	0.134	0.130	0.123	0.112	0.102	0.072
1.00	0.129	0.139	0.140	0.134	0.127	0.117	0.102	0.088	0.052
1.20	0.138	0.144	0.141	0.133	0.123	0.109	0.090	0.071	0.030
1.40	0.146	0.148	0.143	0.130	0.116	0.099	0.075	0.054	0.007
1.60	0.153	0.152	0.142	0.126	0.108	0.086	0.061	0.035	−0.016
1.80	0.159	0.153	0.142	0.121	0.100	0.075	0.044	0.016	−0.040
2.00	0.166	0.155	0.139	0.115	0.090	0.061	0.028	−0.005	−0.065

TABLE 49B

Interpolated values of $-\log \gamma$ for mixtures of acetic acid and sodium acetate
(After Cohn, Heyroth and Menkin (1928))
Temperature 18°C.

IONIC STRENGTH OF ACETATE SOLUTION	MOLE FRACTION OF TOTAL ACETATE AS CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\log \gamma$								
μ									
0.02	0.065	0.061	0.061	0.060	0.059	0.059	0.058	0.058	0.056
0.04	0.088	0.082	0.080	0.078	0.077	0.077	0.075	0.075	0.071
0.06	0.105	0.095	0.092	0.090	0.089	0.088	0.086	0.085	0.080
0.08	0.118	0.106	0.102	0.099	0.098	0.096	0.094	0.093	0.087
0.10	0.129	0.114	0.110	0.106	0.105	0.103	0.101	0.099	0.092
0.12	0.138	0.120	0.115	0.112	0.110	0.108	0.105	0.103	0.095
0.14	0.146	0.126	0.120	0.116	0.114	0.112	0.109	0.107	0.098
0.16	0.153	0.130	0.124	0.119	0.117	0.114	0.111	0.109	0.099
0.18	0.159	0.134	0.127	0.123	0.120	0.117	0.114	0.111	0.101
0.20	0.166	0.139	0.131	0.126	0.123	0.120	0.116	0.114	0.102
0.40	0.202	0.155	0.142	0.134	0.130	0.125	0.120	0.116	0.098
0.60		0.155	0.139	0.128	0.123	0.117	0.110	0.105	0.083
0.80		0.147	0.127	0.115	0.108	0.101	0.093	0.088	0.063
1.00					0.090	0.083	0.074	0.067	0.040
1.20								0.045	0.015
1.40								0.021	−0.011
1.60								−0.005	−0.038
1.80									−0.065

In table 48B are values of pK' at different ionic strengths. In the above example the ionic strength is given by $\dfrac{(0.3)\,(2)^2 + 0.8}{2}$ = 1.0. Interpolation in table 48B gives pK' = 6.650.

For acetate systems there may be used the equation:

$$pH = 4.73 + \log \frac{[\text{Acetate}]}{[\text{Acetic acid}]} + \log \gamma$$

if the Sørensen value of the "0.1 N calomel half-cell" is used; or

$$pH = 4.77 + \log \frac{[\text{Acetate}]}{[\text{Acetic acid}]} + \log \gamma$$

if the value of the "0.1 N calomel half-cell" corresponding to 0.3357 at 18° is used.

In either case values of log γ are given in tables 49A and 49B.

CHAPTER X

Outline of the "Hydrogen Electrode" Method

Let a noble metal, such as gold or platinum, be coated with platinum black or palladium black. Let this metal be placed in a solution containing hydrogen ions, under a definite partial pressure of hydrogen.

This combination of metal, hydrogen and solution constitutes a hydrogen half-cell, commonly called a "hydrogen electrode."

When two such half-cells are placed in liquid junction, as illustrated in figure 36, a complete cell is formed. Its metallic terminals will exhibit an electrical potential difference at E. This can be measured by imposing an electromotive force of opposite direction and of such magnitude as to prevent current flowing through the cell in either direction. This, the potentiometric method, is described in Chapter XVI.

It will be convenient to regard the potential difference at E, between the metals, as the algebraic sum of potential jumps at the interface between each metal and the contiguous solution and of a potential jump at the liquid junction (L of figure 36).

There is no general and at the same time simple way in which this liquid junction potential can be related to the composition of the two solutions. However, there is good reason to believe that the interposition of a saturated solution of potassium chloride will greatly *reduce* the magnitude of this liquid junction potential. For present purposes we shall make the bold assumption that this device reduces the liquid junction potential to a small constant value. Indeed we shall regard this value to be so small as to be negligible in the first consideration.

With this understood, we have left for our consideration the two potential-jumps at the metal-solution interfaces. Such an interface is called an *electrode*. With the understanding that a potential-jump or potential difference is meant, we may speak of an electrode potential.

An electrode potential cannot be used for our present purposes unless it be obtained under conditions which we call equilibrium

conditions.   These are discussed in later chapters.   Here we shall assume that they exist.

There is no sure way of measuring the value of the potential-jump at any single electrode.   Therefore, an arbitrary standard hydrogen half-cell is selected and its electrode potential is called zero.   When this is done the potential of the whole cell is allocated to the half-cell which is joined to the standard.
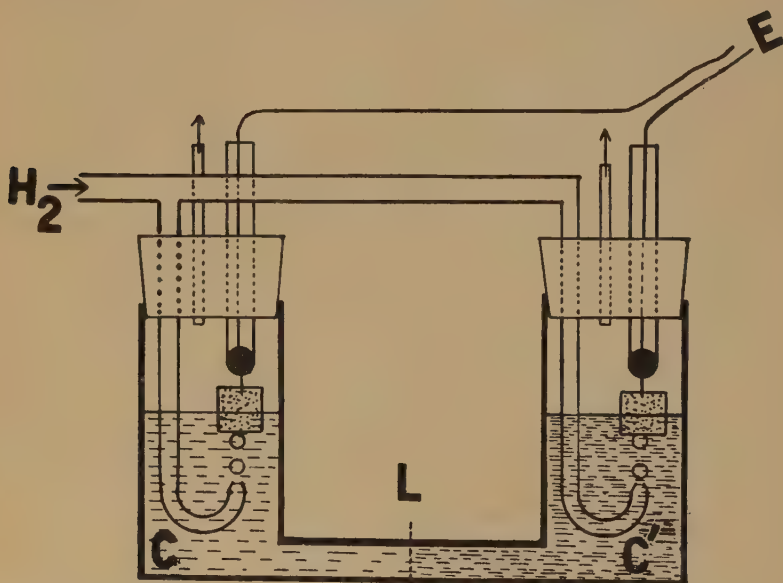
FIG. 36. DIAGRAM OF TWO HYDROGEN HALF-CELLS IN LIQUID JUNCTION AT L

For historical reasons the nature of this arbitrary standard hydrogen half-cell is defined in a manner which it is very difficult to conform to experimentally.   We shall dodge the discussion of this standard for the present.   We shall simply refer to it as the "normal hydrogen half-cell" and shall assume that someone has constructed it and has instituted a series of direct comparisons with other hydrogen half-cells.

Suppose, for instance, that a solution tenth molar with respect to acetic acid and tenth molar with respect to sodium acetate has been used in a hydrogen half-cell with one atmosphere of hydro-

gen and in conjunction with the "normal hydrogen half-cell."
It has been found that at 18°C. the E.M.F. of this cell is 0.267
volt and that the platinum on the acetate side is negative to the
platinum of the "normal hydrogen half-cell." If we agree to
call the potential of the normal hydrogen electrode zero and to
give the sign of the metal to the potential of the other electrode
we may speak of the potential on the acetate side as −0.267
volt. Potentials so referred to the normal hydrogen half-cell
are indicated by the subscript h in E_h.

The hydrogen half-cell with the "standard acetate" solution
can now be used as a secondary working standard. Suppose
solutions a, b and c are to be studied. They are placed in turn
at position X in a cell described as follows.

$$\text{Pt, H}_2(1 \text{ atmos.}) \left| \begin{array}{c} \\ \text{X} \\ \end{array} \right| \begin{array}{c} \text{KCl} \\ \text{sat.} \end{array} \left| \begin{array}{c} 0.1 \text{ N Acetic acid} \\ 0.1 \text{ M Na Acetate} \end{array} \right| \begin{array}{c} \text{H}_2, (1 \text{ atmos.}) \\ \text{Pt} \end{array}$$

A   B   C   D
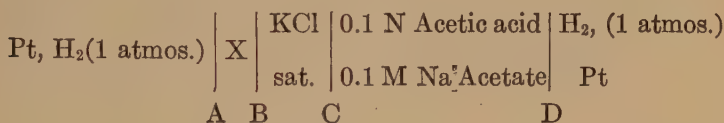
This reads: Platinized platinum under one atmosphere pressure
of hydrogen is placed in contact with solution X. The latter is
separated by a saturated solution of KCl from the mixture of
0.1 N acetic acid and 0.1 M sodium acetate. In the latter solu-
tion is a platinized platinum electrode under one atmosphere of
hydrogen. Potential-jumps occur at A, B, C and D.

We have agreed to neglect the potential differences at B and C.
We have agreed to accept the value $E_h = -0.267$ at 18° for the
potential at D.

When solutions a, b and c are in turn placed at X the electro-
motive forces are, for example, those indicated in the last column
below.

E.M.F. of cell for   "Potential"   "Electrode"   Cell   E.M.F. of Cell
  standardization
(standard acetate) E_h

                          0   "normal hydrogen"
        0.267   − 0.156   a   0.111
                      − 0.267   "standard cell"   0.200
                      − 0.467   b   0.501
                      − 0.768   c

It is obviously necessary to determine whether the platinum of electrode a, for example, is positive or negative relative to the platinum in the "standard acetate." It is then a simple matter to arrange the "potentials" E_h relative to that of the normal hydrogen electrode in the correct order. See figure 40, page 259.

It is obvious that, so far as a comparison between two solutions is concerned, the selection of a standard is of no consequence. The difference between electrodes b and c is 0.301· volts with b positive to c and this difference remains whatever the ultimate standard of reference. However, if we are to agree upon the meaning of numerical values assigned to single electrodes, agreement on a standard is necessary.

Each of the "potentials" in the above set of examples may be considered characteristic of the solution. As such these potentials would suffice for many correlations with the degree to which the property of a substance placed in these solutions appears.

For historical reasons these potentials themselves are not used. Instead any such potential, E_h, is divided by $-0.000,198,322$ T where T is the absolute temperature $(273.1 + t°C. = T)$. Values for this expression at various temperatures centigrade are found in appendix C, page 674.

The result of this division is called pH.

$$\frac{E_h}{-0.000,198,322\ T} = pH \tag{1}$$

Thus for the potentials given in the above series we have the following values of pH.

POTENTIAL AT 18°C. E_h	pH
0	0
−0.156	2.70
−0.267	4.62
−0.467	8.09
−0.768	13.30

USE OF CALOMEL HALF-CELLS

In the previous section cells composed of two hydrogen half-cells were considered. It is usually more convenient to use as a

working, or comparison, half-cell a so-called calomel half-cell. Such half-cells are described in Chapter XV. The types in widest use are the half-cell in which 0.1 N KCl solution is used and the half-cell in which saturated KCl is used. The latter is the more convenient; the former the better standardized. In each instance pure mercury is the metal of the electrode and pure calomel (Hg_2Cl_2, usually written HgCl) is present in solid form.

The beginner is advised to use the following cell

$$\text{Pt, H}_2 \text{ (1 atmosphere)} \left| \text{Solution X} \right| \begin{matrix} \text{KCl} \\ \text{(sat.)} \end{matrix} \left| \begin{matrix} \text{KCl, HgCl} \\ \text{(sat.)} \end{matrix} \right| \text{Hg}$$

A	B	C
Hydrogen half-cell	Connecting solution	"Saturated calomel half-cell"
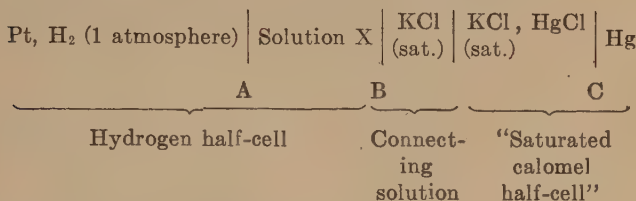
In the first instance solution X is made one of the standards described in Chapter XXIV. For convenience certain values assigned to A are given on page 672.

With these values at A accepted, a measurement of the E.M.F. of the cell permits the calculation of the sum of the potentials at B and C. This is to be used as the working standard and the potential at B is to be considered not to vary as solution X is changed. Then as solution X is changed the value at A can be calculated from the potential of the whole cell and the standardized value of B + C. A standardized value for pH is then calculated as follows.

$$\frac{\text{E.M.F. of cell—Potential (B + C)}}{0.000,198,322\ T} = \text{pH}$$

For example: The observed E.M.F. is 0.648 volt. Potential B + C has been found by the process of standardization to be 0.246 volt. The temperature is 25°C. (25° + 273°.1 = 298°.1 = T). Hence

$$\frac{0.648 - 0.246}{0.05912} = 6.80 = \text{pH}$$

OUTLINE OF PROCEDURES

Although it is impracticable to describe at this point the details of a complete system for the measurement of hydrogen ion concentration, an outline may be given with which to coordinate the main features as they will develop in subsequent chapters.
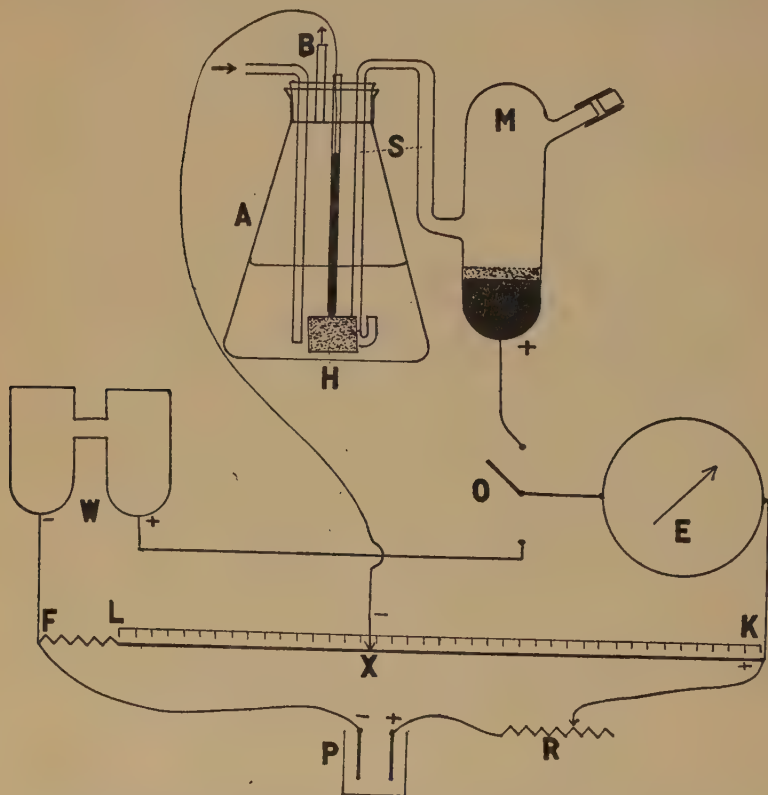
Fig. 37. A Simple Arrangement for Potentiometric Measurement of pH

Figure 37 illustrates a simple system which may be put together from inexpensive material. It is not a system which can be recommended for even rough measurements, but it will work and is well adapted to show the principles concerned.

Hydrogen, prepared by one of the methods described in Chapter

XVII passes into the hydrogen electrode vessel A and escapes at B. Connected with this vessel by the siphon S, filled with a saturated KCl solution, is the calomel electrode M consisting of a layer of mercury covered by calomel under a saturated solution of KCl. The hydrogen electrode H consists of a piece of platinum foil covered with platinum black. It is welded to a platinum wire which is sealed into the glass tube.

Hydrogen is bubbled through the solution in A until solution and electrode are thoroughly saturated with the gas.

The difference between the potential at the mercury-calomel junction and the potential at the hydrogen electrode is now measured by means of a potentiometer. A simple form of this is illustrated.

A storage battery P sends current through the rheostat R, the calibrated resistance-wire K-L and the fixed resistance L-F. By properly setting the switch O a Weston cell W having an electromotive force of 1.018 volts can be connected to K and F, the + pole of the Weston cell being connected to the + side of the battery current. The rheostat R is now varied until there is no deflection of the galvanometer or electrometer E. Then the difference of potential between K and F is equal to the E.M.F. of the Weston cell. The resistance K-L is such that when the above adjustment is made the difference of potential between K and L is one volt. A scale properly divided is placed beside the wire K-L. When the sliding contact X is at K there will be no difference of potential between X and K. When X is at L the difference of potential between X and K will be one volt. When X is at some intermediate position the difference of potential between X and K will be that fraction of one volt indicated by the scale.

After the potentiometer is adjusted by means of the standard Weston cell, the switch O is thrown to connect the calomel electrode-hydrogen electrode system and X is slid in one direction or the other until the galvanometer E shows no deflection. Then the difference of potential between X and K is equal to the difference of potential between mercury and platinum.

The temperature is read and the data put into the equation given above.

Neither measured E. M. F. nor Weston cell should be left in

circuit for more than an instant.   While switch O can be used
for this momentary completion of circuit, it is more convenient
to use a telegraph key in the galvanometer circuit.

If care be taken to maintain the hydrogen at barometric pres-
sure, the effects of minor variations of the barometer from sea
level conditions and of displacement of hydrogen by water vapor
may be neglected in rough measurements.   A discussion of the
barometric pressure is found in Chapter XII.

In all cases where two unlike solutions are joined as in figure 36,
there will develop a local potential difference at the liquid junction.
To deal with this precisely is the most difficult of the problems
encountered.   The subject is discussed in Chapter XIII.   In
very many instances, however, the employment of a saturated
solution of KCl, as is specified in the apparatus illustrated in
figure 37, reduces the liquid junction potential difference to an
order of magnitude which is negligible.

Since variations may occur in the calomel electrode or in the
reliability of the hydrogen electrode it is well to check the system
frequently by means of measurements made with the standard
solutions previously mentioned.

In the use of the potentiometer the elementary principles
must be understood lest standard cells or half-cells be injured
or quite erroneous results obtained.   Therefore, these principles
are discussed in Chapter XVI.

Were it not for the fact that several experimenters have tried
to make hydrogen electrode measurements by use of conductivity
instruments, it would seem hardly necessary to say that the
measurement of conductivity or its reciprocal, resistance, is a
procedure entirely different from the measurement of electro-
motive forces or potential differences.[1]

If the beginner is puzzled by the array of apparatus described
in the following pages he may welcome the following suggestion.
The main outline of a problem can often be defined by the use
of the immersion electrode used in connection with the saturated
calomel half-cell and by using as a potentiometer the voltmeter

[1] The surprising number of cases in which this confusion has been re-
vealed may be an interesting psychological result of the emphasis hitherto
placed upon conductivity measurements, sometimes to the entire exclusion
of any reference to potentiometric measurements.

system. This set of apparatus is illustrated on page 325. It not infrequently happens that the outlining of a problem with this or a comparable system will indicate that further refinement would be useless or confusing. It also frequently happens that the errors suggest phantom relations or obscure existing relations of importance. It is, therefore, advisable whenever possible to keep the accuracy of measurements just ahead of the immediate demands. To meet this requirement the investigator must gain the ability to judge for himself the apparatus required. It is to contribute toward this and the pleasure of work that the following chapters are written in some detail. If the reader does not care to work out the peculiar requirements of his problem he is advised, after having outlined his problem with the system mentioned above, to obtain a reliable potentiometer of standard, not unique, design and to use the system illustrated on page 295. In the first instance accurate temperature control is unnecessary. In the second instance it is advisable if for no other purpose than the avoidance of vexatious uncertainties.

CHAPTER XI

On Changes of Free-Energy

. . . . in our measurements of nature the rules of operation are in our control to modify as we see fit, and we would certainly be foolish if we did not modify them to our advantage according to the particular kind of physical system or problem with which we are dealing.—BRIDGMAN.

From two points of view it is advisable for those who undertake the determination of hydrions to review those aspects of thermodynamics which are of more immediate importance to the subject. In the first place, the equations which are used are fundamentally of thermodynamic origin; and, if they are to be applied intelligently, their meaning should be appreciated. In the second place it will be of interest to see how a consideration of energy changes and means of their measurement may illuminate a rather gloomy aspect of our previous treatment of equilibria. At the very origin of the derivation of the equilibrium equation which we have been using, the statement was made that the equilibrium constant could remain a constant only while the environment remained constant. Strictly this is, of course, an impractical condition. Every change in the concentration of the reacting species, as well as every change in the amount of extraneous matter present, is a change of the environment. We were content to ignore this while surveying the larger features of the subject. We were content to ignore it because a judicious selection of cases made it appear that our neglect is of secondary importance. But even then we soon encountered aggravating discrepancies. The equilibrium constant for acetate solutions of only moderately varying composition appeared to vary appreciably. The equilibrium of an indicator system seemed to change with addition of neutral salts. We may well believe that part of each discrepancy is attributable to forces which we shall not be able to evaluate even with the aid of the more complete equations. However, a considerable part of the discrepancies encountered will be shown to

arise from the attempt to apply approximate equations to data the precision of which warrants more elegant formulation.

The approximate equation is based upon the conduct of the "ideal" gas. Since this equation not only is extensively used but also serves as a model, its derivation will be given first. There will then follow a presentation of equations which are more strictly applicable to the actual systems which we know do not behave in a manner comparable with that of an ideal gas, or ideal solute.

APPLICATION OF THE LAWS OF AN "IDEAL" GAS

For the sake of simplicity imagine two aqueous solutions, one containing sugar at the molar concentration $[S]_1$ and the other containing sugar at the molar concentration $[S]_2$. Let these solutions be under the same external pressure and be separated by a semipermeable membrane, permeable to the water but not to the sugar. Let the membrane be movable. The sugar in solution at the higher concentration will drive the membrane before it, there will be a tendency toward the equalization of sugar concentrations and, if the membrane be under restraint, work will be expended in overcoming force.[1] By this trivial presentation there is suggested a crude analogy with the tendency toward equalization of concentrations when two vessels of gas at different pressures are connected and with the mechanical work which the process of equalization can do. In this analogy originates one manner in which energy changes are related to the accompanying material changes. The comparatively simple gas laws are rather directly applied to solutes.

There may first be considered the simple fact that a gas can absorb energy as heat and, by the resulting expansion, expend energy as mechanically measurable work. Imagine the gas, initially at volume V_1, to be held under the constant pressure, P, of a frictionless piston of cross-sectional area A. Let the gas be heated until it shall have expanded to volume V_2. The piston will then have been pushed through a *distance* determined by the value of $\dfrac{V_2 - V_1}{A}$ or $\dfrac{\Delta V}{A}$. Now the product of area, A, and pres-

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[1] The reader should not interpret this as a description of the mechanism.

sure, P, gives the magnitude of the *force* which the expanding gas has to overcome.   Also

$$\text{force} \times \text{distance} \equiv \text{work}$$

Hence;

$$\text{work} = (PA) \frac{\Delta V}{A} \text{ or } W = P\Delta V \qquad \cdots \quad (1)$$

If the heat added is more than equivalent to the work done, the difference is attributed to an increase of internal energy, U.   If Q is heat added and W is work done by the system we write

$$\Delta U = Q - W \tag{2}$$

We shall find that differences of energy so defined have perfectly definite values for definite changes of state.

Now let it be assumed that the gas is an "ideal" gas, one specification for which is that its internal energy per mole is determined by the temperature alone.   Then ΔU may be made zero by maintaining this gas at constant temperature.

But although W will now equal Q its magnitude may range widely.   If, for instance, the opposing pressure of the piston be always maintained during the expansion at a value much less than the pressure of the gas, it is obvious that not all the work possible to obtain will be gotten.   The *maximum work* will be obtained when the opposing, outside pressure differs from the internal pressure by an infinitesimal.

Under these conditions of maximum work let the second specification in the definition of an "ideal" gas be applied, namely rigid conformity to relation (3) which, it will be recalled, is an expression of the laws of Boyle and Gay-Lussac.

$$PV = nRT \tag{3}$$

P is the pressure in atmospheres, V is the volume in liters, n is the number of moles of the gas, R is the gas constant, and T is the absolute temperature.[2]

For one mole of gas

$$PV = RT \tag{3a}$$

[2] See page 245.

At constant temperature, the pressure-volume relation will be described by some isotherm on a P:V diagram such as the isotherm of figure 38. Starting at P_1V_1 (A of the figure) the gas, expanding against the external pressure $P_1 - dP$ (dP being an infinitesimal) increases in volume to the extent of the *infinitesimal* dV. The work done is $(P_1 - dP)\, dV$. But since the product of the infinitesimals, namely $(dP)\,(dV)$, is negligible compared with $P_1 dV$,

$$dW = P_1 dV \tag{4}$$

At the new pressure $P_1 - dP$ let the process be repeated and finally let the infinitesimal steps be repeated an infinite number of
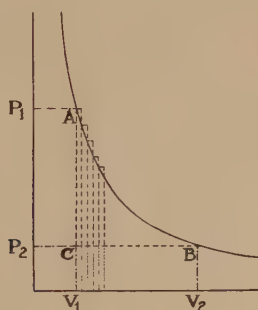
FIG. 38. ISOTHERMAL PV-CURVE FOR A "PERFECT GAS"

times (as suggested crudely by the steps of the figure) until the gas has been brought to V_2 and P_2 at B. Then the work which will have been performed will equal the area ABC. To formulate this the method of the integral calculus must be used.

At each step $dW = PdV$. Find the sum of all steps between V_1 and V_2; that is, integrate (5) as indicated, between the limits V_1 and V_2.

$$W = \int_{V_1}^{V_2} PdV \tag{5}$$

Since P is variable it must be found in terms of V from the relation $PV = nRT$.

$$W = \int_{V_1}^{V_2} nRT \frac{dV}{V} = nRT \int_{V_1}^{V_2} \frac{dV}{V} \tag{6}$$

The integral is

$$W = nRT \, ln \, \frac{V_2}{V_1}$$

Or, since for an ideal gas $P_1V_1 = P_2V_2$,

$$W = nRT \, ln \, \frac{P_1}{P_2} \tag{7}$$

In these equations ln (*logarithmus naturalis*) symbolizes (natural) logarithm to the base e.

Equation (7) states by symbols and tacit implications that the maximum work capable of being performed by a perfect gas, absorbing heat from its surroundings but kept at constant temperature, is equal to the product of the number of moles of gas n, the gas constant R, the absolute temperature of the gas T, and the natural logarithm of the ratio of the initial and final pressures.

Next imagine a dilute solution of some substance, for which the osmotic pressure can be calculated from the ideal gas equation, $PV = nRT$.

Without having to repeat the reasoning applied in the case of the gas and without necessarily having to bring forth a specific device which will perform work while the substance is being brought from one solution to another, we may at once apply equation (7) specifying that in this application the pressures are the osmotic pressures of the dissolved substance in question. In general, wherever we have a substance which we assume is conducting itself as an ideal gas or ideal solute and this substance is transferred between two pressures P_1 and P_2, we may write:

$$W = RT \, ln \, \frac{P_1}{P_2} \tag{8}$$

for the reversible work of isothermal transfer of one mole of substance. If concentrations of the substance A are proportional to the respective pressures

$$W = RT \, ln \, \frac{[A]_1}{[A]_2} \tag{9}$$

The work, W, if expressed in electrical terms, is **nFE**. E is the faraday, **n** is number of faradays required to effect the trans-

fer of one mole and **E** is the electrical potential. Hence equation (9) may be written

$$\mathbf{E} = \frac{\mathrm{RT}}{\mathbf{nF}} \, ln \, \frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} \tag{10}$$

Thermodynamics presents this proximate equation to the experimentalist and leaves it to his ingenuity first to devise an experimental means of applying it and next to determine whether the assumptions regarding the chemical transformations, which take place in this particular device, are met. In Chapter XII a device is described and conditions specified whereby it is believed that equation (10) is applicable to the determination of the ratio between two hydrogen ion concentrations. The specific equation is

$$\mathbf{E} = \frac{\mathrm{RT}}{\mathbf{F}} \, ln \, \frac{[\mathrm{H}^+]_1}{[\mathrm{H}^+]_2} \tag{11}$$

where the electrical work term **EF** is used since the device is supposed to furnish this work by flow of electricity.

It is now our duty to note that the most fundamental and most dangerous assumption which led to equation (11) was that the hydrogen ions obey the laws of the ideal solute. It should be evident in the rather fair harmony of the subject matter presented up to this point that data based ultimately upon the conduct of the hydrogen electrode and interpreted through the simple equation (11) have not distorted the picture very severely. Indeed there is a rough analogy between the picture we have drawn and a map of an area drawn with the assumption that the needle of the compass points true north. There are, as it were, local perturbations with every solution. True and apparent concentrations become as far apart as north pole and magnetic pole in certain cases; but local navigation remains possible.

The laws of an ideal gas may be considered as limiting laws to which the conduct of the actual substance approaches under simple conditions. What then prevents their general application? It appears that, to make these laws applicable, the size of the molecules would have to approach the mathematical point and there would have to be no cohesive or other forces of inter-action. In the case of ions the electrostatic forces of interaction appear

to far outweigh other matters in their interference with the applicability of the gas laws. We, therefore, face an extremely complex problem.

Not only should account be taken of deviations from the gas laws due to the inherent nature of the solute, but the solvent surely cannot be considered merely as an invariant environment.

But let us take under consideration two solutions of the substance A at concentrations $[A]_1$ and $[A]_2$. At extremely high dilutions variations of the solvent's properties with variation of the concentration of the solute tend to vanish and the solute is highly dispersed. Then equation (10) holds for transfer of A from one low concentration to another in a medium of nearly constant properties. If conditions are not simple, equations (9) to (11) will not hold. We may than introduce corrections. For concentration $[A]_1$ let the deviation in energy be ω_1 and for $[A]_2$, ω_2 etc. Equation (12) describes the experimental data.

$$W = RT \, ln \frac{[A]_1}{[A]_2} + \omega_1 - \omega_2 \qquad (12)$$

The ω terms are merely the correction terms expressed in the dimensions of energy. If we wish to express the corrections in terms of factors to be applied to the concentrations, substitute $RT ln \gamma_1$ for ω_1 and $RT ln \gamma_2$ for ω_2. Then we have (13) or (14)

$$W = RT \, ln \frac{[A]_1}{[A]_2} + RT \, ln \frac{\gamma_1}{\gamma_2} \qquad (13)$$

$$W = RT \, ln \frac{[A]_1 \, \gamma_1}{[A]_2 \, \gamma_2} \qquad (14)$$

A term such as $[A]_1\gamma_1$ may now be considered as a "corrected concentration," and may be called the *active* concentration or *the activity*. γ is the *activity coefficient*.

The symbol a is usually used for *activity*. We shall *parenthesize* a chemical symbol when we signify the activity of the substance whose symbol is inclosed in the parentheses, just as we use *brackets* to signify the *concentration* of the substance whose symbol is enclosed in brackets. Then

$$W = RT \, ln \frac{(A)_1}{(A)_2} \qquad (15)$$

Now we have an equation of the *form* of that derived from the ideal gas laws and can proceed to all the mathematical developments which have already been made with the gas laws.

This legitimate juggling does scant justice to the subject, for by following the route to the same final equation (15) which was followed by Lewis (See Lewis and Randall, *Thermodynamics* and references therein to early papers by Lewis), we shall encounter some useful ideas.

THE FREE ENERGY EQUATION

It is a principle of thermodynamics that the total energy, E, of a system in a given state will return to the same value if the system be put through a cyclic process and be returned to the first state. Likewise if a system be known in two states and if we designate the total energy in the one case by E_1 and in the other case by E_2, we may speak of the increment of total energy $\Delta E = E_2 - E_1$ or of an infinitesimal increment dE. This will be measurable in the sense that we can speak of dE as being determined by the heat added, dq, and by the work, dw, done by the system according to the equation:

$$dE = dq - dW \tag{16}$$

The negative sign is given to dW, as it occurs in (16), to signify energy *lost from* the system because of the work *done by* the system.

Temporarily we shall use another quantity called the entropy, S. In theory any system can, by means of reversible processes be put through any desired changes and then be returned to its first state. It will then have the original value of the entropy, all changes in the entropy of the system being measured by the equation

$$dS = \frac{dq}{T} \tag{17}$$

Equations (16) and (17) give (18)

$$dE = TdS - dW \tag{18}$$

In the measurement of energy changes there is occasion to distinguish certain quantities which it is a convenience to name. The quantities are:

E + PV = H, called "the heat content"
E − TS = A, called "the free energy" by Helmholtz
E − TS + PV = F, called "the free energy" by Lewis.

Distinction between H, A and F should be kept clear. We shall use only F and shall refer to it without qualification as the free energy.

$$F = E - TS + PV \qquad (19)$$

By differentiation

$$dF = dE - TdS - SdT + PdV + VdP \qquad (20)$$

Combine (20) and (18).

$$dF = - SdT + VdP - dW + PdV \qquad (21)$$

At constant temperature and pressure $dT = 0$ and $dP = 0$. Hence

$$-dF = dW - PdV \qquad (22)$$

In (22) PdV is what may be called the hydrostatic work done by any change of volume at pressure P. Hence the decrease in free energy, $-dF$, attending a reversible change of state, *measured at constant temperature and pressure*, may be described as the maximal non-hydrostatic work, $dW - PdV$. The following treatment will be limited throughout by the understanding that temperature and pressure are to remain constant. Hence we shall speak only of changes of free-energy, and can eliminate from consideration A, and H.

Consider a system made up of several components. If to this system there be added an infinitesimal mass, dm_a, of component A, all other conditions remaining the same, we may say that the energy of the system is increased by the addition of chemical energy. The increase of the energy of the system per unit (any unit) increase of the mass of the given component will be defined by

$$\frac{dE}{dm} = \mu$$

where μ is called the chemical potential of the given substance in the system considered. If we choose the molecular weight as the unit of mass of component A, and indicate by N_a the number of moles

$$\frac{dE}{dN_a} = \mu_a$$

Gibbs shows that if the temperature and pressure of the system be kept constant and the masses of all other components be kept constant

$$\left(\frac{dF}{dN_a}\right)_{T, P, N_b, N_c\ldots\ldots\ldots} = \mu_a \qquad (23)$$

dF being the increase of free energy. The subscripts T and P are reminders of constancy of temperature and pressure and the subscripts N_b, N_c . . . . . indicate constancy of the masses of other components.

But

$$\left(\frac{dF}{dN_a}\right)_{T, P, N_b, N_c\ldots\ldots\ldots}$$

is what Lewis calls the partial molal free energy, $\bar{F}_a$, of component A. Hence

$$\bar{F}_a = \mu_a = \left(\frac{dF}{dN_a}\right)_{T, P, N_b, N_c\ldots\ldots\ldots} \qquad (23a)$$

As a solution is diluted its solute tends to conform closer to the conduct of an ideal solute. As a *limiting* law we can state for solute A

$$\mu_a = \bar{F}_a = RTln\,[A] + B \qquad (24)$$

Here B is a function of temperature and is a constant at a fixed temperature. But being a limiting law (24) cannot be applied in general. However, the convenient form of this equation can be preserved by substituting for the concentration [A] a defined quantity as will presently be done.

We are quite accustomed to think of the flow of heat as determined by the relative temperatures of the bodies between which

heat-exchange takes place. " . . . . we may imagine every-thing to have a certain tendency to lose heat, or we may say that heat has a tendency to escape from every system. Temperature is then a measure of this escaping tendency of heat." (Lewis and Randall, *Thermodynamics*). In the same way we may think of the escaping tendency of a real substance, for example water. If the escaping tendency of water is the same for the water in a solution as it is for the water in the vapor phase above the solu-tion, water will not of itself pass from the one phase to the other. If the escaping tendency of the water is greater in one phase than in a second, water will pass from the first phase to the second. So it is in general for any *substance*.

Gibbs (1878) had shown that the chemical potential, μ, has these properties.

As a concrete measure of escaping tendency there is liberty to choose any measure which is convenient. Vapor tension might be chosen; but true partial vapor pressures are not generally meas-ured. The so-called fugacity (symbol f) is used as a suitable measure. For solute A we may define its fugacity by the equation

$$\mu_a = \overline{F}_a = RTln\, f_a + B \qquad (25)$$

At extreme dilution

$$\mu_a = \overline{F}_a = RTln\, [A] + B = RTln\, f_a + B \qquad (26)$$

But (25) holds at any concentration. For two states of a sub-stance at constant temperature, the states being indicated by subscripts 0 and 1, we have

$$\mu_1 = RTln\, f_1 + B \qquad (27)$$

$$\mu_o = RTln\, f_o + B \qquad (28)$$

or

$$\mu_1 - \mu_o = RTln\, \frac{f_1}{f_o} \qquad (29)$$

Now choose one state of the substance as standard and let its fugacity be f_o. The relative fugacity, $\dfrac{f_1}{f_o}$ will be called *the activity*, a_A. Then

$$\mu_1 - \mu_o = RTln\, a_A \qquad (30)$$

We shall now represent the activity of any substance by a paren-
thesis placed about the symbol for the substance.   For example
(A) is the activity of substance A, e.g.,

$$\mu_1 - \mu_o = RTln\ (A)$$

If then two states of a solute A are being compared and both differ
from the standard state chosen,

$$\mu_1 - \mu_2 = RT\ ln\ \frac{(A)_1}{(A)_2} \tag{31}$$

Comparison with (14) and (15) shows that activity is related to
concentration by introducing the coefficient γ called the *activity
coefficient*.   From the above we have:

$$\Delta F = \bar{F}_1 - \bar{F}_2 = \mu_1 - \mu_2 = RT\ ln\ \frac{[A]_1\ \gamma_1}{[A]_2\ \gamma_2} = RTln\ \frac{(A)_1}{(A)_2} \tag{32}$$

THE EQUATION FOR CHEMICAL EQUILIBRIUM

Equation (23) is

$$\mu_a = \frac{dF}{dN_a}$$

or

$$\mu_a\ dN_a = dF$$

with the understanding that temperature and pressure are con-
stant and that all other components are constant while an in-
finitesimal change is made in component A.   Even though all
other components are subject to change, the initial or the final
state of a system of components a, b, c . . . . n may be described by

$$F = N_a\mu_a + N_b\mu_b + N_o\mu_o \ldots . N_n\mu_n \tag{33}$$

Suppose we have a chemical reaction in which N_a moles of con-
stituent a and N_b moles of constituent b are transformed to N_r
moles of constituent r and N_s moles of constituent s.
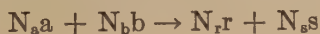
$$N_a a + N_b b \rightarrow N_r r + N_s s$$

Before the reaction

$$F_1 = N_a\mu_a + N_b\mu_b \tag{34}$$

After the reaction

$$F_2 = N_r\mu_r + N_s\mu_s \tag{35}$$

That we may have a definite basis of reference, let F_o represent the free energy of a system in which the components are in a selected standard state indicated by subscript 0.

$$F_{o1} = N_a\mu_{ao} + N_b\mu_{bo} \tag{36}$$

$$F_{o2} = N_s\mu_{so} + N_r\mu_{ro} \tag{37}$$

$$F_1 - F_{o1} = N_a(\mu_a - \mu_{ao}) + N_b(\mu_b - \mu_{bo}) \tag{38}$$

$$F_2 - F_{o2} = N_r(\mu_r - \mu_{ro}) + N_s(\mu_s - \mu_{so}) \tag{39}$$

But by (30)

$$\mu_a - \mu_{ao} = RTln\ (a)$$
$$\mu_b - \mu_{bo} = RTln\ (b)$$
$$\text{etc.}$$

Hence

$$F_1 - F_{o1} = RTln\ (a)^{N_a}(b)^{N_b} \tag{40}$$

$$F_2 - F_{o2} = RTln\ (r)^{N_r}(s)^{N_s} \tag{41}$$

$$- \Delta F_{1,2} - (- \Delta F_o) = F_1 - F_2 - (F_{o1} - F_{o2}) = - RT\ ln\ \frac{(r)^{N_r}(s)^{N_s}}{(a)^{N_a}(b)^{N_b}} \tag{42}$$

But $F_{o1} - F_{o2}$, the difference of free energy of the systems with components in the standard states, is a constant, K'. For convenience put $K' = RTln\ K$.

$$- \Delta F_{1,2} = RT\ ln\ K - RT\ ln\ \frac{(r)^{N_r}(s)^{N_s}}{(a)^{N_a}(b)^{N_b}} \tag{43}$$

At the state of equilibrium we have such values of $(r)^{N_r}$, $(s)^{N_s}$, etc. in (43) that no change occurs and $-\Delta F_{1,2} = 0$. Hence,

$$RT\ ln\ K = RT\ ln\ \frac{(r)^{N_r}(s)^{N_s}}{(a)^{N_a}(b)^{N_b}}$$

or

$$\frac{(r)^{N_r}(s)^{N_s}}{(a)^{N_a}(b)^{N_b}} = K \tag{44}$$

In (44) K is the ordinary mass action constant for the equilibrium equation in which activities have been substituted for concentrations.

Likewise for the equilibrium of the reversible reaction

$$HA \rightleftharpoons H^+ + A^-$$

we may write

$$\frac{(H^+)\,(A^-)}{(HA)} = K_a \tag{45}$$

instead of the approximate equation

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a' \tag{46}$$

By introducing activity coefficients as described on page 236, we also have

$$\frac{[H^+]\,\gamma_{H^+}\,[A^-]\,\gamma_{A^-}}{[HA]\,\gamma_{HA}} = K_a \tag{47}$$

To illustrate the applications of these equations, cases will be introduced at appropriate places in the subsequent development. To relieve the subject of the rather artificial aspect it has now attained, there will be given in outline in Chapter XXV the theory which Debye and Hückel have proposed as a partial explanation of those deviations from the laws of an ideal solute which are observed with solutions of ions.

It has become evident in the derivation of the equilibrium equation by means of free energy changes that we have abandoned the use of concentrations except as they may be introduced by the device of the relation

$$[A]\gamma_a = (A)$$

This is a great convenience because custom has established the use of the balance and volumetric flask as a means of defining the composition of solutions. However, we should not lose sight of

the fact that there is a certain degree of artificiality involved in this manner of relating states to concentration.   Were the measure of free energy changes as easy as weighing, the sprinkling of a substance into a solution until the partial free energy balances some standard might prove as useful in many instances as the current practice of weighing and measuring.   *Indeed this is what has actually happened in very many applications of the hydrogen electrode to problems of biochemistry and industry.*   A phenomenon unrelated in any known way to anything measurable by balance or volumetric flask is related to the so-called pH value of the solution.   When the method of measuring the pH value is analyzed it is found to be a measurement of a free energy change.   The "hydrion concentration," which pH is supposed to represent, and the not very successful attempt to standardize by reference to a "normal potential" are introductions which are not essential but which are used to satisfy our constant desire to relate degree of action to mass.[3]

In other words the free energy equation has its own intrinsic value capable of standardization and use without reference to mass and capable of describing systems *in terms of the direction and extent of the flow of energy* when these systems are allowed to react upon one another.

Of course, this not satisfying.   The aim of science is to relate all properties and all phenomena.   The convenience of laboratory practice demands the use of the balance, and molecular theory urges us to take account of particle number.   Nevertheless it is well to overemphasize the above aspect for a moment lest too slavish attention to the more customary formula introduce terms which are often unnecessary.

$$\text{NUMERICAL VALUES FOR } 2.3026 \, \frac{RT}{F}$$

In the practical application of electromotive force measurements and in numerical calculations for theoretical purposes there are

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[3] It might be said at this point that it is easy to imagine a process controlled by automatic potentiometric methods and that it would be only adding unnecessary complexities to translate the electromotive force into artificial terms.

occasions to use the numerical value of $\dfrac{RT}{F}$ at a given value of the absolute temperature, T. Furthermore equations of the form

$$E = \frac{RT}{F} \, ln \, \frac{(H^+)_1}{(H^+)_2} \tag{48}$$

are more frequently used with Briggsian instead of Naperian logarithms as:

$$E = 2.3026 \, \frac{RT}{F} \, log_{10} \, \frac{(H^+)_1}{(H^+)_2} \tag{49}$$

We, therefore, desire values of $2.3026 \, \dfrac{RT}{F}$. R is the gas constant, T is the absolute temperature ($273°.1 + t°C$), and F is the faraday.

In making numerical solutions of this equation it is essential to use a set of consistent units for the quantities concerned. Before these are discussed it may be noted that the values in current use for x in the relation

$$\frac{RT}{F} \, ln(\quad) = xT \, log_{10}(\quad)$$

differ from one another by an amount too small for the difference to be of much significance in physical applications. On the other hand the differences between some of the extreme values are such that discrepancies as large as 0.6 millivolt[4] appear in certain common calculations. Since it is irritating to have to take account of such unnecessary discrepancies in calculations which form the basis for the comparison of experimental data, it is desirable to adhere to a well standardized value which incidentally shall have more digits than may be necessary to develop the actual significance of measurements. *International Critical Tables*

[4] Comparison of six well-known texts shows, as extremes of the value of x, 0.0001983 and 0.0001985. For t = 25°C., (T = 298.1°), xT is 0.059113 in the first instance and 0.059173 in the second. The calculated difference of potential between a hydrogen electrode in a solution of pH = 0 and a hydrogen electrode in a solution of pH = 10 would be 0.59113 volts by the use of the first factor and 0.59173 volts by the use of the second, a discrepancy of **0.6 millivolt**.

now provides accepted values with which the desired value may be reached.

In equation (48) the gas constant, R, is $\dfrac{P_0V_0}{273.1}$ with n = 1 understood.

V_0, the volume of one mole of a perfect gas at 0°C., is 22412 milliliters when the pressure is one atmosphere, 45° latitude. In distinction from this pressure, the *normal atmosphere* (A_n) is defined as the pressure exerted by a vertical column of liquid 76 cm. long, density 13.5951 grams per cubic centimeter, acceleration of gravity being 980.665 centimeters per second per second. The atmosphere at 45° latitude (A_{45}) is assumed to be related to the normal atmosphere (A_n) as

$$\log_{10}\frac{A_n}{A_{45}} = 0.000,021,4$$

Also one milliliter = 1.000,027 cubic centimeters. Hence V_0 at 0°C. and one normal atmosphere is 22411.5 cubic centimeters.

P_0, to be consistent with the above, is to be regarded as one normal atmosphere and it may here be remarked that, when the value we are now developing is to be applied to the barometric correction for the hydrogen electrode, the pressure should be, strictly speaking, in terms of the normal atmosphere.

$P_0 = 980.665 \times 76 \times 13.5951 = 1,013,250$ dynes per square cm. Then

$$R = \frac{1,013,250 \times 22,411.5}{273.1} = 83,150,684 \text{ ergs per degree per mole.}$$

International Critical Tables rounds the value off to 8.315×10^7 since it is not more accurately known, but, since the stated logarithm (which will probably be used in calculations) corresponds to 8.31507×10^7 we shall continue with the latter value.

One joule absolute = 10^7 ergs.

One joule absolute = one volt-coulomb (abs).

Hence R = 8.31507 volt-coulombs (abs).

International Critical Tables accepts as a basic constant one faraday = 96500 coulombs (abs). Hence equation (48), with **E** to be stated in absolute volts, is

$$E = \frac{8.31507}{96500} T \, ln \, \frac{(H^+)_1}{(H^+)_2}$$

Transposing to common logarithms (base 10) by multiplying with the modulus 2.302585, we have:

$$\mathbf{E} = 0.000198406 \; T \log \frac{(H^+)_1}{(H^+)_2} \tag{50}$$

The units employed up to this point have been those of the absolute system for which the fundamental constants are the centimeter, the gram and the second (cgs-system). Most actual measurements of potential difference ($\mathbf{E}$) are not made in terms of absolute volts but are usually supposed to be made in terms of the so-called international volt. This is a quantity derived by means of Ohm's law [$\mathbf{E}$ (in volts) = current (in amperes) $\times$ resistance (in ohms)] from the following *definitions* of the international ohm and of the international ampere.

The *international ohm* is the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area and of a length of 106.300 cm.

The *international ampere* is the unvarying electric current which, when passed through a solution of nitrate of silver in water in accordance with specification II (of the 1908 London conference), deposits silver at the rate of 0.00111800 gram per second.

Consequently the *international volt* (by Ohms' law) is the electrical pressure (electromotive force) which, when steadily applied to a conductor the resistance of which is one international ohm, will produce a current of one international ampere.

Notwithstanding this definition the socalled international volt in actual use is derived from sets of Weston standard cells maintained by national standards laboratories. In agreement with the London conference of 1908 the "saturated" Weston cell (see page 342) is considered to have an electromotive force of 1.01830 international volts at 20°C. This is virtually the definition of a new unit and according to *International Critical Tables* it "furnishes a subsidiary definition which is slightly discordant with the primary one." Therefore *International Critical Tables* distinguishes between conversion factors which are based on the defined value of the Weston cell and which are designated by (v)

and conversion factors based on the defintions arising from the performance of the silver coulometer and designated by (a).

> One international volt (v) = 1.00042 absolute volt.
> One international volt (a) = 1.00045 absolute volt.

Before making a transformation of equation (50) by the use of one of these conversion factors we shall discuss two questions concerning which there may be some curiosity.

The first concerns the faraday. It might appear that, when the international ampere is once defined, the introduction of the accepted value 107.880 as the atomic weight of silver would furnish $\dfrac{107.880}{0.00111800} = 96493.7$ international coulombs as the *derived* value of what might tentatively be called the "international faraday." But in the definition of the international ampere it is well understood that the word "silver" refers to the gross deposit. (For the inadequacy of the specifications see Bureau of Standards circular *60*, pp. 34 to 36 and Bureau of Standards Bulletin *13*, 499.) Hence, if care be taken to distinguish between the use of the above derivation as one of several experimental evaluations of the faraday and its use as a definition of a new quantity (tentatively called "international faraday") it will be appreciated that the latter use is inconsistent with the concept of the faraday as a quantity not subject to legislative definition. This is the attitude of International Critical Tables.[5]

Accordingly *International Critical Tables*, expressing the magnitude of *the* faraday (the only unit of that name which is recognized) in terms of the various units, states first its *accepted basic constant;*

> one faraday = 96500 absolute coulombs

and then the conversion factors

> one faraday = 96510 international coulombs (v)
> one faraday = 96507 international coulombs (a)

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[5] According to personal correspondence with Dr. N. Ernest Dorsey, Associate Editor, *International Critical Tables* whom I thank for several very helpful comments on this section.

The second question concerns the choice between the conversion factor for absolute to international volts (v) and the conversion factor for absolute to international volts (a). Were there a definite prospect of an immediate revision of the defined value of the Weston cell, reestablishing the true international volt as that to be in actual use, it would be wise to employ the (a) conversion factor. However certified values for the Weston cells in use are in terms of the international volt (v) and while the matter is one of very minor physical significance it seems more consistent with practice to use the factor 1.00042.

Hence

$$E = 0.000,198,322 \ T \log \frac{(H^+)_1}{(H^+)_2} \qquad (51)$$

in international volts (v).

A table of values for 0.000,198,322 T will be found in the Appendix, page 674.

Since electromotive force measurements furnish data for the calculation of free energy changes it is desirable to have equation (49) in the form

$$E\,F = RT \log \frac{(H^+)_1}{(H^+)_2}$$

A numerical form of this, consistent with the derivations given above, is;

$$\text{Joules (abs)} = 96500 \ E \ \text{(abs)} = 19.1462 \ T \log \frac{(H^+)_1}{(H^+)_2} \quad (52)$$

$$\text{Gram calories (15°)} = 4.575 \ T \log \frac{(H^+)_1}{(H^+)_2} \qquad (52a)$$

96500 E (abs. volts) = joules absolute
96510 E (international volts (v)) = international joules (v)
23058.5 E (abs. volts) = gram calorie (15°C.)

The last is derived by use of the conversion factor one gram calorie (15°C.) = 4.185 absolute joules.

In the above discussion no attention was paid to the uncertainties of the basic constants because such questions do not enter

the use of a factor in preserving uniformity in calculations. However, if there are introduced the estimated uncertainties tabulated in *International Critical Tables*, we find that F is uncertain by about one part in 10,000 and R by about 0.9 part in 10,000 (from the uncertainty of V_0).

Hence the factor in equation (51) is

$$\left\{ \begin{array}{l} 0.000,198,322 \\ \pm 0.000,000,038 \end{array} \right\}$$

T_0 is uncertain by not over $0°.15$, or 5.5 parts in 10,000. Hence, in Appendix C, A at $0°C$. is uncertain by about $5.5 + 1.9 = 7.4$ parts in 10,000; or at $0°C$.

$$A = \left\{ \begin{array}{l} 0.054162 \\ \pm 0.000040 \end{array} \right\} \qquad \frac{1}{A} = \left\{ \begin{array}{l} 18.4631 \\ \pm 0.0014 \end{array} \right\}$$

Likewise, at $30°C$, A is uncertain by about $4.9 + 1.9 = 6.8$ parts per 10,000 or

$$A = \left\{ \begin{array}{l} 0.060111 \\ \pm 0.000041 \end{array} \right\} \qquad \frac{1}{A} = \left\{ \begin{array}{l} 16.6357 \\ \pm 0.0011 \end{array} \right\}$$

On the other hand if we are concerned with *precision* of potential measurements only, a precision to within ± 0.0001 volt in an observation requires the use of the fifth decimal place in A (appendix C) to maintain uniformity of statement consistent with such observational precision.

CHAPTER XII

Theory of the Hydrogen Electrode

One of the oldest unsolved problems in physical chemistry is the source of E.M.F. in the simple galvanic cell and the mechanism of its production.—RIDEAL.

There are two aspects of the theory of the hydrogen electrode which may well be kept distinct. One is the problem of its mechanism. The other is its application to the measurement of the free energy change in the transfer of hydrions from one concentration to another. A complete solution to the first is not attained. The second is a matter of thermodynamics and, to the extent that we can detect the actual factors that must be taken into account, our formulations are safe if made by the all too general methods of thermodynamics.

We shall studiously avoid any attempt to discuss the mechanistic aspect, and shall refer only to those few of many papers on the subject which are found in *Transactions of the Faraday Society*, Vol. 19 (1924). On the other hand it will be necessary to introduce one or another concept of the gross aspect of the electrode mechanism in order to meet the elementary requirements of thermodynamics. The reason for this is simple. Thermodynamics provides the formulation of *a* cell reaction: but, before this rather ethereal generalization can be applied, the data of the analyst, of inorganic or organic chemistry and the deductions of the physical chemist regarding the states of substances in solution must be assembled to provide some knowledge of the concrete components of a system that are to be dignified by a place in the equation. Such data need only inform us of the initial and final products of the cell reaction; and because we are then concerned in no essential way with the true path of the reaction or with intermediate products we cannot be said to be dealing fundamentally with the mechanism. By the same token we are at liberty to employ artificial hypotheses of intermediate stages if it adds anything to the convenience of our formulation; for we

realize at the introduction of these hypotheses that they are matters of convenience only and are destined from the first to be eliminated from the final equations.

We shall first consider Nernst's (1889) concept of electrolytic solution tension as a useful way of remembering certain important relations.

If a metal be placed in a solution of its salt there will be a difference of electrical potential between metal and solution which will vary in an orderly manner with the concentration of the metal ions. To account for the difference of potential Nernst assumed that a metal possesses a characteristic solution tension comparable with the vapor pressure of a liquid, or better, with the solution pressure of a crystal of sugar—but with the important qualification that it is the metal ions which pass into solution. Imagine first that the metal is in contact with pure water. The metal ions passing into solution carry their positive charges and leave the metal negative. Thus there is established a so-called double layer of electrical charges at the interface between metal and solution, the solution being positively and the metal negatively charged relative to one another. This potential difference forcibly opposes further dissolution of metallic ions, for the relative positive electrical field in the solution and the relative negative field in the metal restrain any further migration of positively charged ions from the metal to the solution. Equilibrium is established when the electrostatic control equalizes the solution pressure.

If now there are already in the solution ions of the metal, fewer ions will escape from the metal and the metal is left more positive.

Therefore the higher the concentration of the positive metallic ions in the solution the more positive will be the charge on the metal and, conversely, the lower the concentration of the metallic ions in the solution the more negative will be the charge on the metal.

Not only metals but various gases are found to act in a similar way when means are devised to bring them into a situation as easily handled as are metal electrodes. Hydrogen is one of these gases and the means of handling it as an electromotively active gas is to take it up in one of those metals such as platinum, pal-

ladium or iridium which in a finely divided condition hold large
quantities of hydrogen. Platinum black deposited upon plati-
num and laden with hydrogen forms a hydrogen electrode. It
can be brought into equilibrium with hydrogen ions as silver is
brought into equilibrium with silver ions; and the more positive
it becomes the higher must be the concentration of the positively
charged hydrogen ions in the surrounding solution.

The metal-metal ion system is only a special case of a system
the components of which differ by one or more electrons. Such
systems are called oxidation-reduction systems. The system
$H_2 : H^+$ is one of these. If we assume an electron escaping
tendency for this system, we can formulate the relation between
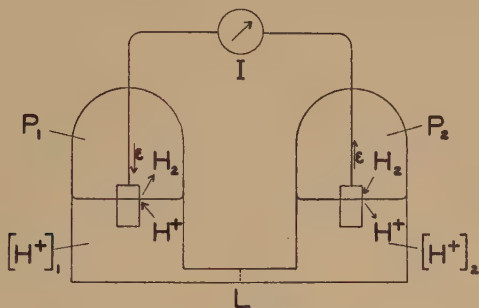
FIG. 39. DIAGRAM OF TWO HYDROGEN HALF-CELLS IN LIQUID
JUNCTION AT L

I, current indicating instrument when cell is allowed to run or poten-
tiometer when E. M. F. is to be balanced.

the cell's electromotive force and the material changes by the
method developed in Chapter XVIII.

Let us now operate with the cell depicted in figure 39, where
one solution of hydrion concentration $[H^+]_1$ is under the hydrogen
pressure P_1 and the other solution of hydrion concentration
$[H^+]_2$ is under the hydrogen pressure P_2. As is usual in the
application of the thermodynamic formulation we have to *assume*
that we know enough about the mechanism of the cell to describe
its main function. The end result, which is all we need to know,
is the lowering of hydrogen pressure and the raising of hydrion
concentration on one side, the raising of hydrogen pressure and
the lowering of hydrion concentration on the other side, and the

accompanying flow of a definite electric current. We will *assume* in this instance that hydrogen will pass from the gaseous phase on one side to yield electrons to the metal and to produce new hydrions; that the electrons flow through the exterior metal connections to the electrode in the other solution and that there they add to hydrions and form new hydrogen molecules.

Instead of allowing the cell to run down (with the expenditure of electrical energy and the approach to equalization of hydrogen pressure and hydrogen ion concentrations) we balance the electromotive force of the cell potentiometrically. We then *assume* that any compensating adjustments in the distribution of the other ions which would have to accompany the changes in hydrion concentration play no direct part in the electrode conduct and that events at the liquid junction (L, fig. 39) are to be handled by the method of Chapter XIII.

From the theory presented in Chapter XI we know that if we have hydrions in two solutions at concentrations $[H^+]_1$ and $[H^+]_2$ and if we assume that the ideal gas laws, relating temperature, pressure and concentration, are obeyed, the free energy change ΔF for the transfer of one gram mole of hydrogen ions from the higher concentration, $[H^+]_1$, to the lower concentration, $[H^+]_2$, is formulated by the relation:

$$- \Delta F = \text{RT } ln \frac{[H^+]_1}{[H^+]_2} \tag{1}$$

A similar relation holds for the transfer of one gram mole of hydrogen gas from pressure P_1 to pressure P_2, or, for one *equivalent* of hydrogen,

$$- \Delta F = \text{RT } ln \frac{\sqrt{P_1}}{\sqrt{P_2}} \tag{2}$$

The energy *lost from* the system is equal to the *work done by* the changing system under the conditions of maximum work. If the work which would be done by the current, were the cell allowed to run, is expressed in electrical terms we have

$$- \Delta F = \mathbf{EnF} \tag{3}$$

where $\mathbf{E}$ is the electrical pressure or electromotive force that we measure in volts by the potentiometric method (see Chapter XVI)

F is the faraday, the quantity of electricity associated with one electrochemical equivalent and n is the number of electrochemical equivalents.

Then equation (1) gives that part of the free energy change associated with the virtual transfer of hydrions; or by using equation (3) with (1) and assuming $n = 1$,

$$EF = RT \, ln \, \frac{[H^+]_1}{[H^+]_2} \tag{4}$$

A second portion of the work is concerned with the changing hydrogen pressure, and for one equivalent of hydrogen

$$E'F = RT \, ln \, \frac{\sqrt{P_1}}{\sqrt{P_2}} \tag{5}$$

But on any one side the hydrogen pressure tends to decline and the hydrion concentration to rise when electrons flow from this side; on the other side the hydrogen pressure tends to rise and the hydrion concentration to decline as electrons flow in. Hence on any one side the effect of a change in hydrogen pressure is opposite to that of a change in the same direction on the part of hydrogen ion concentration. The total work is the difference:

$$EF - E'F = RT \, ln \, \frac{[H^+]_1 \sqrt{P_2}}{[H^+]_2 \sqrt{P_1}} \tag{6}$$

If the hydrogen pressure is the same on both sides, and is maintained so, we have:

$$EF = RT \, ln \, \frac{[H^+]_1}{[H^+]_2} \tag{7}$$

As explained in Chapter XI, and as noted above, the measurement must be made under conditions of maximum work. This is fulfilled when the cell is not allowed to run but is held with its electromotive force nicely balanced by a potentiometer (see Chapter XVI). It is the electromotive force (E. M. F.) of the cell as if on open circuit that is measured and called E of the above equations. Separating E we have from (7)

$$E = \frac{RT}{F} \, ln \, \frac{[H^+]_1}{[H^+]_2} \tag{8}$$

We have continued up to this point with the assumption that the hydrions obey the laws of an ideal gas.   Actually they do not do so strictly and therefore, if we are to be strict in the application of the equation, we should substitute for concentrations the corresponding *activities* of the hydrions.   The FORM of the equation then remains the same.   See the previous chapter.   Thus at constant hydrogen pressure

$$E = \frac{RT}{F} \, ln \, \frac{(H^+)_1}{(H^+)_2} \qquad (9)$$

Here it will be recalled that we use parentheses to indicate activity just as we use brackets to indicate concentrations.

It will also be recalled that in Chapter XI attention was directed to the simple proposition of using the hydrogen electrode potentials themselves as the data characteristic of solutions. With only a formal modification, this is what is done in a comparative way when some solution is given an arbitrary hydrion activity of unity, other solutions are compared with it and the data are thrown into the form which at 25°, for example, will be

$$\frac{E}{0.05912} = \log \frac{1}{(H^+)}$$

Compare with

$$\frac{E}{0.05912} = \log \frac{1}{[H^+]} = pH$$

The significance of the equation for the "concentration" chain is that, if T is known, and if the activity of the ions in the other solution is known, then the activity of the ions in one solution can be determined from the E. M. F. of the chain.   Fundamentally there is no other way of applying electromotive force determinations to the estimation of ion activities, unless there can be brought to bear mass action relations.   This makes it necessary to start somewhere in the system with a solution whose hydrogen ion activity has been determined by an independent method.

But let us assume the concentration formulation and let us assume for the moment that the conductivity method will give us correct information upon the hydrogen ion concentration of some simple solution such as that of HCl.

It will be remembered that hydrogen ion concentrations are expressed in terms of normality, a solution normal with respect to hydrogen ions being one which contains in one liter of solution 1 gram[1] of hydrogen ions.

If, then, the normality of the hydrogen ion concentration in any unknown solution is to be determined it would seem that the most convenient solution with which to compare the unknown would be a solution of normal hydrogen ion concentration. Between a hydrogen electrode in this standard and a hydrogen electrode in the unknown solution of hydrogen ion normality $[H^+]_x$ there would be a difference of potential, E given by the equation:

$$E = 0.000,198,322 \, T \log \frac{1}{[H^+]_x} \tag{10}$$

A measurement of E and T would give $[H^+]_x$. Now E in the above equation is the difference between the potential difference at the one hydrogen electrode and the potential difference at the other hydrogen electrode. Nothing need be known about the value of either single potential difference and very little is known. If the electrode in the normal solution is made the standard it is obviously convenient for present purposes to call the potential difference between this electrode and the solution zero. Thus arose the definition:

The potential at a hydrogen electrode under one atmosphere pressure of hydrogen in a hypothetical solution normal with respect to the hydrogen ion shall be considered to be zero at all temperatures.[2]

To conform to the use of "activity" this may be modified to:

The potential at a hydrogen electrode under one atmosphere pressure of hydrogen in a solution of unit hydrion activity shall be considered to be zero at all temperatures.

The term "normal hydrogen electrode" is now associated with the latter definition.

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[1] It makes little difference whether we regard the atomic weight of hydrogen as 1.0 or as 1.008 for the purpose at hand.

[2] In various places, notably in the report of the Potential Commission of the Bunsen-Gesellschaft (Abegg, Auerbach and Luther, 1910) it is not specifically stated that this difference of potential shall be *zero at all temperatures*, but it seems to have been so understood and is specifically so stated by Lewis (1913).

Having established by definition the value of the potential difference at the "normal hydrogen electrode" it becomes convenient to speak of the potential difference at any other hydrogen electrode as the hydrogen electrode *potential,* thus abbreviating the term "potential difference." It is, of course, implied that such a "potential" is referred to the potential difference at the normal hydrogen electrode. To indicate this the symbol E_h is used.

Unfortunately the standard solution would have to be prepared by means of "strong" acids and the estimation of the hydrogen ion activity would fall under those uncertainties which we shall leave to Chapter XXIII for discussion. In the meantime we shall assume that a well established standard is available and that this conforms to the demand of the rigid equation for which the standard should be unit activity instead of the unit concentration. With this we could proceed to the comparison of all solutions applying directly the formula which relates the E. M. F. of a "concentration cell" to the ratio of activities (or for approximate purposes to concentrations). But it is more convenient to substitute for the standard a "working standard" known as the calomel half-cell. (See Chapter XV.) When this is joined to a hydrogen half-cell we need to know the potential difference between the calomel half-cell and the ultimate hydrogen standard. Then we can correct the observed E. M. F. by this difference and can consider the corrected E. M. F. to be as if it were that between two hydrogen half-cells for which we have the above formula.

We have continued with the assumption that there is no difference of potential in a cell other than those at the electrode-solution interfaces. As a matter of fact a potential difference arises wherever too unlike solutions are put in liquid junction. The importance of this and the attendant difficulties are the occasion for a separate chapter on the subject. See Chapter XIII.

ON THE SIGN OF ELECTRODE POTENTIALS

Convention in regard to signs will be discussed again in Chapter XVIII. Here it may be said that we shall use the convention to be used by *International Critical Tables*. The metal of the

Also the change of potential of the quinhydrone electrode with change
of pH (see Chapter XIX). Also positions of arbitrarily assigned poten-
tials of 0.1 N and saturated calomel half-cells (see Chapter XXIII).
Compare this figure with table A, Appendix.
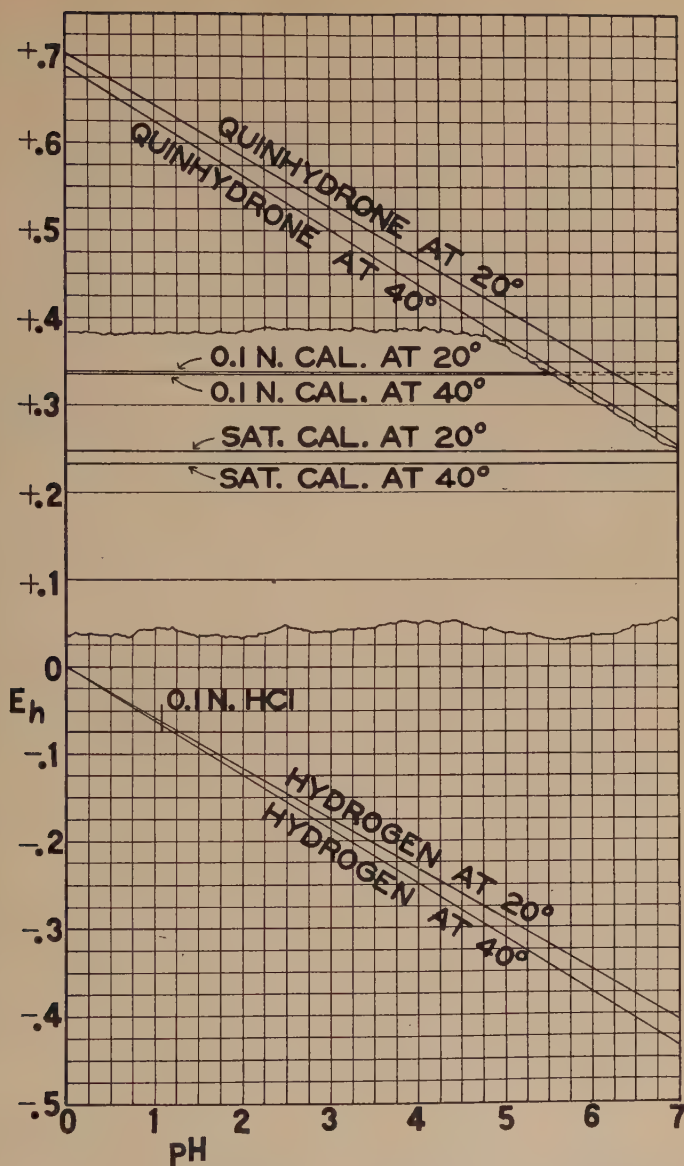
hydrogen electrode then appears to become more negative as the pH value of the solution increases. Figure 40 shows this relation and also the orientation of the potential of the metal of a hydrogen electrode in a solution of any pH relative to the potential of the mercury of calomel half-cells.

BAROMETRIC CORRECTIONS

While we included at one point the effect of varying hydrogen pressure we continued the later discussion under the assumption that the hydrogen electrode is operating with one atmosphere pressure of hydrogen. If the hydrogen pressure varies from this, the above equation is incomplete. Instead of reincorporating the hydrogen pressure in the working equation it is more convenient to deal with a variation of hydrogen pressure as a correction.

The potential difference between a metal and solution will vary somewhat with the condition of the metal. A hammered, twisted or scratched electrode may show a different potential against a given concentration of its ions than will an electrolytically deposited metal. In the case of the hydrogen electrode it seems to make little difference whether the hydrogen be held in platinum, palladium or iridium but it does make a considerable difference if the surrounding pressure of hydrogen varies. If we have two hydrogen electrodes immersed in the same solution at the same temperature but under different pressures of gaseous hydrogen, we may assume that the concentration of the hydrogen in one electrode is different from that in the other electrode, and that the potential difference may be expressed as

$$E_b = E_1 - E_2 = \frac{RT}{nF} \, ln \, \frac{[H]_1}{[H]_2} \tag{11}$$

in which equation R, T, n, and F have their customary significances and $[H]_1$ and $[H]_2$ are concentrations of *atomic* hydrogen in the electrodes (platinum black). Since n is 1, it may be omitted.

We may now assume that there is an equilibrium between the molecular hydrogen about the electrode and the atomic or ionic hydrogen in, or issuing from, the electrode. This equilibrium may be expressed in accordance with the mass law as follows:

$\dfrac{[\text{H}] \times [\text{H}]}{[\text{H}_2]} = \text{K}$ where $[\text{H}]$ = concentration of atomic hydrogen

and $[\text{H}_2]$ = concentration of molecular hydrogen

Whence,

$$[\text{H}] = \sqrt{\text{K}[\text{H}_2]} \tag{12}$$

Substituting (12) in (11), we have

$$\text{E}_b = \frac{\text{RT}}{\text{F}} \, ln \, \frac{\sqrt{\text{K}\,[\text{H}_2]_1}}{\sqrt{\text{K}\,[\text{H}_2]_2}} = \frac{\text{RT}}{2\text{F}} \, ln \, \frac{[\text{H}_2]_1}{[\text{H}_2]_2}$$

It should be noted that the factor 2 in this equation does not come from giving hydrogen an effective valence of 2, as has often been stated, but from the introduction of equation (12).

If the ratio of pressures is equal to the ratio of gas concentrations

$$\text{E}_b = \frac{\text{RT}}{2\text{F}} \, ln \, \frac{\text{P}'_{\text{H}_2}}{\text{P}_{\text{H}_2}}$$

If P'_{H_2} be one atmosphere and P_{H_2} be expressed in atmospheres

$$\text{E}_b = \frac{\text{RT}}{2\text{F}} \, ln \, \frac{1}{\text{P}_{\text{H}_2}} \tag{13}$$

This is the equation for the difference of potential between a hydrogen electrode under one atmosphere pressure of hydrogen (e.g., the normal hydrogen electrode) and a hydrogen electrode under pressure P_{H_2}.

Experimental justification of this equation is found in the experiments of Wulf, Czepinski, Lewis and Rupert, Lewis and Randall, Lewis and Sargent, Ellis, Loomis and Acree and others.

Hainsworth, Rowley and MacInnes (1922, 1924) have studied the effect of pressures up to 1000 atmospheres and taking account of the volume changes of Hg, calomel, etc. which are negligible for smaller differences in pressure, they find a linear relation up to 100 atmospheres.

Several writers have felt constrained to emphasize the fact that in determining the hydrogen pressure from barometer readings they have subtracted the vapor pressure of the solution. The

emphasis is still advisable, for a considerable number of precise hydrogen electrode data are published with corrections for barometric pressure on the basis that the normal hydrogen electrode pressure is one atmosphere *including* the vapor pressure of the solution. Corrections should be made to one atmosphere pressure of *hydrogen,* or else the standard used should be distinctly specified.

Clark and Lubs (1916) used the commonly accepted "standard condition" of à gas which is the concentration at 0°C. and 760 mm. pressure. Their final values were not thereby rendered incomparable with other's values since the correction was applied to the standard as well.

In applying the correction,

$$E_{bar.} = \frac{RT}{2F} ln \frac{1}{P_{H_2}},$$

it will be remembered that a decrease of the hydrogen pressure may be considered as a decrease of the electrolytic solution tension of the hydrogen. Hence under decreased hydrogen pressure the electrode is left more positive. See figure 77, page 387.

In the cell

$$- Pt, H_2 \,|\, H^+ \,|\, KCl, HgCl \,|\, Hg^+$$

if the hydrogen is under diminished pressure the E. M. F. of the cell is too low. Hence the correction must be applied to make the E. M. F. larger than observed. The working equation is then:

$$\frac{E.M.F. + E_{(bar.)} - E_{(calomel)}}{0.000198322\ T} = pH \qquad (14)$$

To aid in the calculation of pressure corrections it is convenient to plot a curve giving the millivolts to be added to the observed E. M. F. for various corrected partial pressures. Tables of corrections from which a chart may be plotted are given in the Appendix. In these tables the barometer pressures given are the corrected pressures. If hydrogen escapes from about the hydrogen

electrode through a trap[3] or other device which exerts back pressure, this pressure must be taken into consideration. Otherwise it is assumed that the pressure of the hydrogen is that of the barometer less the vapor pressure of the solution.

For all ordinary cases it may be assumed that the vapor pressure is that of pure water at the temperature indicated.

If the unit pressure is one atmosphere, the partial pressure must be reduced to atmospheres.

As inspection of the table in the Appendix will indicate, the barometric correction may be neglected in rough measurements. But in very exact measurements it is necessary to make the usual corrections for the barometer reading.

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[3] It is good practice to prevent back diffusion of oxygen by letting the hydrogen escape through a long but not too narrow tube instead of through a trap.

POTENTIAL DIFFERENCES AT LIQUID JUNCTIONS

Until a problem has been logically defined it cannot be experimentally solved.—LEWIS AND RANDALL.

INTRODUCTION

By far the most unsatisfactory aspect of electric cells is the interference of the liquid junction with simple and certain formulation of the electromotive force of the cell. Whenever two solutions of different composition are brought in contact with one another there develops at the junction a potential difference. Since the structure of the junction is not a permanent affair, the ordinary principles of equilibria are difficult to apply. Practically the junction is difficult to reproduce in a manner which will furnish a reproducible potential with solutions of different electrolytes.

So troublesome has this matter proved to be that the tendency in theoretical work is definitely toward the selection of those cells, which, from a practical point of view, have no liquid junction and, from a theoretical point of view, can be formulated as if they had none. An example of such a cell is that described by:

$$- \text{ Pt, } H_2 \text{ (1 atmos.) } | \text{ HCl (0.1M), HgCl (s) } | \text{ Hg } +,$$
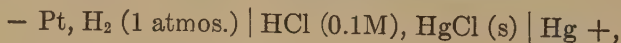
namely, a cell composed of a hydrogen electrode under one atmosphere of hydrogen and a mercury electrode covered by mercurous chloride (solid phase in excess), both in the "same" solution of tenth molar hydrochloric acid.

If, in considering this cell, we were to keep uppermost in mind the principles of oxidation-reduction equilibria (see Chapter XVIII), we might doubt the practicability of the cell, because the difference between the potentials at the two electrodes is so large that we would conclude at once that the mercurous chloride should be reduced by the $H_2:H^+$ system (at the platinum electrode, at least, if not in the solution itself). As a matter of fact

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this difficulty has arisen[1] and the higher, more reproducible potentials of the cell are obtained by a degree of isolation of the solutions about the two electrodes. Then these solutions are made *different*, the one being saturated with mercurous chloride and the other not. Theoretically a liquid junction potential might be present; but, because of their very low concentration, the mercury- and chloride ions in excess upon the one side have no practically significant effect in the liquid junction.

Such cells are sometimes called "cells without liquid junction" or "cells without transference." Those cells in which there occurs a liquid junction which has to be considered are sometimes called "cells with transference."

By ingenious combinations of the data for cells without transference it has been possible in recent years to build a considerable body of important data. But unfortunately the solutions met in the wider applications of cell measurements are so varied that the introduction of liquid junctions is a necessity in the majority of cases. We shall find that such junctions introduce a serious uncertainty into what would otherwise be a most precise account of acid-base equilibria.

In writing the structure of a cell, it is customary to designate the position of a potential difference by a vertical line. When such a potential difference is to be considered as eliminated a double line is used. Thus

$$\text{Pt, } H_2 \mid N/10 \text{ HCl} \mid N/10 \text{ KCl, HgCl} \mid \text{Hg}$$

indicates that there are potential differences at the positions shown by the lines; while if the above chain is written as

$$\text{Pt, } H_2 \mid N/10 \text{ HCl} \parallel N/10 \text{ KCl, HgCl} \mid \text{Hg}$$

the double line indicates that the liquid junction potential difference is to be left out of consideration in formulating the E.M.F., it having been allowed for by some separate treatment.

Scatchard (1925) has departed from this convention by using

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[1] Nonhebel (1926) has not found this difficulty with the silver-silver chloride half-cell.

the double line to indicate a flowing junction.   We shall signify a flowing junction by a waved line, for instance,

$$N/10 \ HCl \wr N/10 \ KCl$$

The flowing junction is described on page 274.

THE CAUSE

The principal cause of the potential difference was attributed by Nernst (1889) to unequal rates of diffusion of ions across the junction.

It has been found in the study of electrolytic conduction that, under uniform potential gradient, different ions move through a solution with different velocities.   The following table taken from Lewis' *A System of Physical Chemistry* shows the velocites of several ions in aqueous solution under a potential gradient of one volt per centimeter.

TABLE 50
Ionic velocities

ION	ABSOLUTE VELOCITY IN CENTIMETERS PER SECOND, 18°C.	ION	ABSOLUTE VELOCITY IN CENTIMETERS PER SECOND, 18°C.
H+.....................	32.50 10^{-4}	OH⁻................	17.80 10^{-4}
K+.....................	6.70 10^{-4}	Cl⁻.................	6.78 10^{-4}
Na+..................	4.51 10^{-4}	NO₃⁻................	6.40 10^{-4}
Li+..................	3.47 10^{-4}	CH₃COO⁻...........	3.20 10^{-4}
Ag+..........	5.70 10^{-4}		

Since, in each case, the potential gradient is the same and the ionic charge the same, it may be inferred that the order in which the velocities stand in the table is the order in which the velocities of free movement will stand.

Let it now be assumed that a solution of hydrochloric acid is placed in contact with pure water of negligible ion content at an imaginary plane surface.   Independently of one another the chloride and the hydrogen ions will *tend* to migrate across the interface and into the water.   As shown in the above table the velocity of the hydrogen ion under the influence of a potential gradient is much greater than the velocity of the chloride ion

under the same gradient, and the relative velocities of free move-
ment must, therefore, be in the same proportion.   Consequently
there will be established on the water side of the plane an excess
positive charge.   This charge will increase until, by the electro-
static attraction the slower moving chloride ions are brought to
the velocity of the hydrogen ions.   When this state is reached,
as it is almost instantaneously, there is established a potential
difference at the liquid junction.   If the water is replaced by a
solution of an electrolyte, we have not only the chloride and the
hydrogen ions migrating across the boundary into this new solu-
tion, but the ions of this solution migrating into the hydrochloric
acid solution.

FORMULATIONS

Before modern requirements led to a reexamination of all the
assumptions entering attempts to formulate liquid junction
potentials it was considered legitimate to operate with free energy
equations expressed with concentrations and with transport num-
bers considered to be independent of the environment.   Merely
as an illustration consider the comparatively simple case where
two solutions of different concentrations of the same binary
electrolyte are placed in contact.

Let the concentration of the ions on one side of the interface
be C and on the other side be a lesser concentration C'.

When migration has established the steady potential E_L let
it be over an interface of such extent that E_L is due to the separa-
tion of one faraday.   If that fraction[2] of the separated charge
which is carried by the anion is n, the work involved in the trans-
port of n equivalents from C to C' is n RT $ln \dfrac{C}{C'}$.   Likewise, if
that fraction of the charge carried by the cations is $1-n$, the
work involved in the transport of $1-n$ equivalents from C to C'
is $(1-n)$ RT $ln \dfrac{C}{C'}$.   The work involved in the *separation* of the
ions as they migrate from the high to the low concentration is

$$E_L F = nRT \ ln \frac{C}{C'} - (1 - n) \ RT \ ln \frac{C}{C'}$$

[2] n = transport number.

Whence

$$E_L = (2n - 1) \frac{RT}{F} ln \frac{C}{C'} \tag{1}$$

Equation (1) was derived on the assumption that, in the formulation of energy changes, concentration ratios can be substituted for activity ratios and on the assumption that the activities of the ions of opposite charge are equal to the corresponding concentration. Omitting these assumptions we would find the equation to be as follows for two solutions of hydrochloric acid

$$E_L = \frac{RT}{F} \left[n_c \, ln \frac{(H^+)_1}{(H^+)_2} - n_a \, ln \frac{(Cl^-)_1}{(Cl^-)_2} \right] \tag{2}$$

Here, as elsewhere in this book, () indicates activity. n_c and n_a are the transport numbers of cations and anions respectively *at the states found*. Equation (2) makes it evident that a complete solution for E_L would require knowledge of the individual ion activities in the two solutions. In this connection we may quote Harned (see page 782 Taylor's *A Treatise on Physical Chemistry*). "Thermodynamics offers valuable aid in the study of liquid junction potentials, but it is not possible by thermodynamic methods alone to evaluate liquid junction potentials, since a knowledge of individual ion activities would be required. We are thus confronted with the interesting perplexity that it is not possible to compute liquid junction potentials without a knowledge of individual ion activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potentials. For the solution of this difficult problem, it is necessary to go outside the domain of exact thermodynamics."

Lewis and Sargent (1909) have treated the special case of two equally concentrated solutions of two different uni-univalent salts having one ion in common. Substituting equivalent conductivities as proportional to mobilities they obtain

$$E_L = \frac{RT}{F} ln \frac{\lambda_1}{\lambda_2} \tag{3}$$

where λ_1 and λ_2 are the equivalent conductivities of two solutions. In their experimental study of cells of the type

$$\text{Ag} \mid \text{AgCl, HCl(c)} \mid \text{KCl, (c), AgCl} \mid \text{Ag.}$$
$$\text{A} \qquad\qquad \text{B} \qquad\qquad \text{C}$$
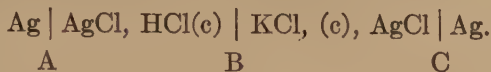
MacInnes and Yeh (1921) assume, for purposes of calculation, that the activities of the chloride ions in the two solutions, of KCl and HCl, are the same when these two solutions have the same concentration, c. Then the potential difference ascribed to A should be the same as that ascribed to C and the electromotive force of the cell should be the liquid junction potential at B.

TABLE 51

Potentials at junctions of solutions of univalent chlorides

25°C.

ELECTROLYTES AT JUNCTION	0.1N SOLUTION		0.01N SOLUTIONS	
	"Observed" MacInnes and Yeh	Calculated Lewis and Sargent's formula	"Observed" MacInnes and Yeh	Calculated Lewis and Sargent's formula
	volts	*volts*	*volts*	*volts*
HCl; KCl	0.02578	0.02840	0.02572	0.02740
HCl; NaCl	0.03309	0.03330	0.03116	0.03190
HCl; NH$_4$Cl	0.02840	0.02860	0.02702	0.02740
KCl; NaCl	0.00642	0.00490	0.00565	0.00450
NaCl; NH$_4$Cl	−0.00424	−0.00460	−0.00426	−0.00450

With this assumption the observed potentials can be compared directly with those calculated by Lewis and Sargent's formula as in table 51.

Scatchard (1925) has calculated the junction potential at A, below, to be 0.0027 volt and at B to be 0.0047 volt.

$$\text{KCl (0.1M)} \; \{ \; \text{KCl (sat.)}$$
$$+\text{A}-$$
$$\text{HCl (0.1M)} \; \{ \; \text{KCl (sat.)}$$
$$-\text{B}+$$
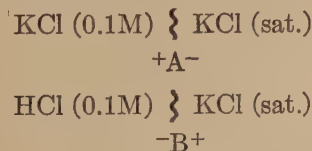
These estimates are of considerable importance to the standardization of pH values as will appear in Chapter XXIII.

Harned (1926) has considered in detail a calculation of the liquid junction potentials at

$$HCl(0.1), KCl(M) \mid KCl \text{ (sat.)}$$

when M is varied from 0 to 3.   He gives the following results.

M	JUNCTION POTENTIAL
	volts
0.0	0.00158
0.3	0.00105
0.5	0.00089
1.0	0.00082
2.0	0.00085
3.0	0.00082

The potentials of liquid junctions between solutions of the same electrolyte at different concentrations are independent of the manner in which the junction is formed provided no membrane is interposed.   In contrast to this the potentials at the junctions of solutions of different electrolytes vary with the manner in which the junction is formed.   If, in addition, the solutions are complex the problem of formulation becomes extremely difficult or impossible of numerical solution.

Among the more important formulations there should be mentioned the following.   Planck (1890) assumed the junction to be initially sharp and mixing to take place by *diffusion*.   Proceeding from Nernst's formulation he reached an equation which has served as a valuable guide.   Johnson (1904) extended the formula to the case where the valences of the ions are not the same. P. Henderson (1907, 1908) treated the case of a *"mixture* boundary," one in which the intervening layer is made up of a series of mixtures of the two solutions in graded proportions.   Cumming (1912) modified the equation by introducing the mobilities of the ions at the different concentrations used.   These and numerous other treatments have been appreciably modified by the realization that it is more consistent with the use of free-energy equations to employ activities in place of concentrations and also by the realization that ion mobilities vary with the nature and concentration of the solution.

What appears to be a comprehensively general treatment has recently been published by Taylor (1927). Of particular importance to our subject is Taylor's development of the idea that, if the electromotive force of a cell with transference is to be formulated rigidly, the cell should be treated as a whole, and that separate treatment of liquid junction potentials must be regarded as a convenient grouping of terms and without physical significance. He pertinently remarks that the electromotive forces of cells commonly used for the determination of pH numbers depend not only upon the activity of the acid but also on the activity of every molecular species and on the mobility of every ion. "If these are sufficiently well known to be allowed for, the acid activity is likely to be sufficiently well known not to need measurement."

To meet the demands of rigid treatment there is very little that can be done with ordinary measurements, but we shall see in a subsequent section that the elementary theory predicts *moderate* success in the *approach to* what may be considered for practical purposes a relatively low, constant liquid junction potential against a solution saturated with KCl. Before this is discussed let us consider certain experimental matters of importance.

METHODS OF FORMING LIQUID JUNCTIONS

For a reason to be discussed in the next section, liquid junctions between solutions of different electrolytes are usually formed by interposing a solution of potassium chloride. Usually this is a saturated solution. Since this saturated solution is frequently the more dense of the two solutions placed in contact it is led to the junction from below.

Experience has suggested the advisability of avoiding junction in capillary spaces (Cumming and Gilchrist, 1923). If a capillary is desired (to delay change of structure at the junction during treatment of a solution) the arrangement indicated in figure 49, page 301, is useful. There a wide liquid junction is found in the bulb. It is protected from the titrated solution by the capillary goose-neck. For bridging between open vessels there is a wide variety of devices of which only a few are shown in figure 41.

Agar saturated with KCl is sometimes very convenient. Michaelis and Fujita (1923) prepare this as follows. Agar (3 grams) is thoroughly melted in 100 grams water. Avoid direct flame. Heat in steam sterilizer or water bath. Add 40 grams KCl and stir gently till dissolved. Pour the mixture while hot into the tube and then cool. Gelfan (1926) described an agar-KCl junction made in a quartz capillary 1–2 microns in diameter.

Wicks have sometimes been used. See, for instance, Michaelis (1914) and Walpole (1914).

Very frequently a membrane, such as parchment or collodion, (cf. Fales and Stammelman, 1923) is used at the junction. There are instances of routine measurements in which this practice is desirable. On the other hand it may seriously complicate the
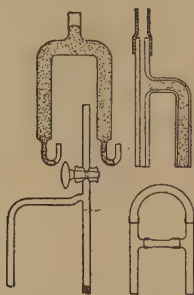
FIG. 41. "SIPHONS" FOR BRIDGES
Upper siphons contain agar-KCl

situation and render more difficult the interpretation of the cell's electromotive force. (Cf. Prideaux and Crooks, 1924.) For the introduction of a membrane is virtually the introduction of a new phase and one junction is replaced by two. Usually the junction potential is increased. This has been accounted for on the assumption of a disproportionate change in the transport numbers of the ions as they enter the membrane phase. In the discussion of non-aqueous solutions there will be a brief sketch of phase boundary potentials and the subject could appropriately be discussed here. However, it is a very large subject with an extensive and highly technical literature. To discuss this for the sake of an adequate presentation of devices which so far have found comparatively little use in the exact application of

the hydrogen electrode would hardly be profitable. It may simply be said that, while the interposition of a membrane is sometimes useful in comparative, routine measurements; it is usually avoided in fundamental studies except of the membrane potential itself. See Michaelis (1926).

Aqueous gels do not have such a serious effect upon relative migration velocities as do membranes such as parchment; but that agar bridges are not in good repute for *exact* work is well known. For instance Lamb and Larson (1920) in speaking of their own use of an agar-KCl bridge remark "Under ordinary circumstances this type of junction would not have been adopted for it does not give the utmost accuracy." But see Michaelis and Fujita (1923) who are of the opposite opinion for a particular arrangement. See page 279.

In their study of transference numbers MacInnes and his co-workers (see MacInnes, Cowperthwaite and Huang (1927), use devices by which a boundary is formed with a shearing motion.

There is good evidence that the potential at a boundary formed by mixture may differ from that at a boundary formed by diffusion. A change in the structure frequently appears in a change of potential with time. For instance, Chanoz (1906) constructed the symmetrical arrangement:

<div align="center">
Electrode MR | M'R' | MR Electrode,
A   B
</div>

and then, by maintaining a more or less sharp boundary at A by renewal of the contact, and allowing diffusion to occur at B, he obtained very definite E.M.F.'s instead of the zero E.M.F. which the symmetrical arrangement demanded. This time effect had been noted by Weyl (1905) and has since been frequently reported, for instance, by Bjerrum (1911), Lewis and Rupert (1911), Cumming and Gilchrist (1913), Walpole (1914) and Fales and Vosburgh (1918).

Since the change of potential has been ascribed to the diffusion or mixing which alters the distribution of the contending, migrating ions, it has seemed to many that the effect could be made more uniform and conditions more reproducible if sand or other material were used to delay mixing and diffusion.

Lewis, Brighton and Sebastian (1917) using Bjerrum's (1911) suggestion of a layer of sand in which to establish the liquid contact found that "at no time were reproducible results obtained nor results which remained constant to 0.0001 volt for more than a minute or two. The potential of the liquid junction first established was surprisingly high (0.030 volt) and fell rapidly without reaching any definite limiting value." The liquids placed in contact in this experiment were 0.1 M HCl and 0.1 M KCl. These authors abandoned the sand method.

On the other hand Myers and Acree (1913) report satisfaction with Bjerrum's "Sandfüllung."

Fales and Mudge (1920) recommend "small cones of cotton wool fitted snugly, but not tightly, into the siphon tubes."

According to Fricke (1924) foreign porous material at the junction may be a cause of error.

Other devices such as the use of a wick have been resorted to, but, on the whole, direct liquid contact is considered the best. There may, however, be occasion when the employment of some restraint is advantageous for rough comparative measurements.

In the description of the system shown by figure 47, page 295, it is stated that liquid junction is formed by first pinching the connecting rubber tube to displace KCl solution, turning the key of the cock and then, by slow release of the pressure on the rubber tube, drawing the solution back into a wide part of the tube. As judged by the reproducibility of cell potentials this gives a satisfactory way of forming a liquid junction.

In 1920 Lamb and Larson described the "flowing junction" which they find to be much more reproducible than the junctions usually made. They conclude "that a 'flowing' junction, obtained simply by having an upward current of the heavier electrolyte meet a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with N solution, gives potentials constant and reproducible to 0.01 of a millivolt."

MacInnes and Yeh (1921) improved the system of Lamb and Larson and confirmed the principle that reproducible liquid junction potentials may be thus obtained, but they find most interesting effects with different rates of flow. Of particular importance

is the observation that the reproducible potentials are not the highest that can be obtained.

The arrangement used by MacInnes and Yeh is shown in figure 42. A and B are reservoirs which supply the two solutions to the junction at J. The rate of flow is adjusted by a screw pinchcock on a rubber tube attached at P. In starting the operation the rubber tip E of a glass rod is pushed into its seat and separates the two parts of the apparatus. The pinchcock at P is closed. The two halves are then filled with their respective solutions and adjusted to the same hydrostatic pressures. P and E are opened and a flowing boundary with sharp definition
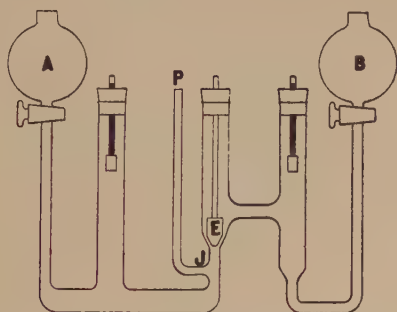
FIG. 42. CELL WITH "FLOWING JUNCTION"
(After MacInnes and Yeh)

forms at J and proceeds along the waste to P. If initial mixing is allowed to take place no amount of flowing will produce constant potentials.

Roberts and Fenwick (1927) use an ingenious device for a flowing junction. It is illustrated in figure 43. "A hole about 1 mm. in diameter is drilled in a thin strip of mica (about 1.5 × 7 cm.) by means of a glass-rod drill, working from both sides of the plate so that the edges are as smooth as possible; it is placed about 5 mm. below the exit tubes of the electrodes. The lower edge of the plate is notched and the faces are painted with hot paraffin, except for a narrow channel (indicated by dotted line) past the hole." A channel leads to one point of the plate on the one side and to the *other point* of the plate on the *other side*. "This insures that the only liquid junction is at the aperture in the plate."

The flowing junction has been applied also by Aten and van Dalfsen (1926), Sørensen and Linderstrøm-Lang (1924) and others. Aten and van Dalfsen allow the intermediate solution to flow through plates of porous alundum.

As Scatchard says, the flowing junction is usually not practical with the hydrogen-half cell "since the change in pressure due to the changing level affects the potential of the hydrogen electrode, and since the junction is disturbed by the rocking or gas bubbling at the hydrogen electrode." Scatchard (1925) says "The flowing junction presumably gives a 'mixture boundary,'—one in which the composition of each infinitesimal layer is the same as though it had been prepared by stirring together the two solutions in the proper proportions, and one which is extremely thin.
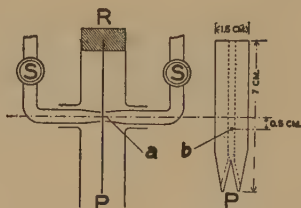
FIG. 43. ROBERTS AND FENWICK'S DEVICE FOR A "FLOWING JUNCTION"

When the flow is stopped the junction changes to a 'diffusion boundary,'—one whose composition is determined by the rates of diffusion of the various ions, which gradually increases in thickness. Any change in the total electromotive force of the cell when the flow is stopped must be due to the difference between the potentials of these two types of liquid junction. Then the effect on the electromotive force of stopping the flow should give some insight into the absolute magnitude of the liquid-junction potential." Scatchard then shows that, with the junction of saturated potassium chloride solution with hydrochloric acid solutions, stopping the flow resulted in a slow increase of the cell potential, the maximum increase being of the same order of magnitude for 1.0 M, 0.1 M or 0.01 M HCl. "Since this difference is almost independent of the acid concentration, it appears that at least the order of magnitude of the potential must be the same in dilute as in concentrated solutions." The difference

was about 0.35 millivolts between the potentials at the "mixture boundary" and the "diffusion boundary." "Both cannot be zero," says Scatchard, "and it is probable that neither is."

POTASSIUM CHLORIDE AS A REDUCER OF JUNCTION POTENTIAL

A very excellent illustration of the proposition that "a problem cannot be experimentally solved until it is logically defined" arose from the theory of Nernst that the junction potential is due to the unequal tendencies in the migration of ions. The table of velocities given on page 266 will show that if KCl is concerned, no large potential can arise from the participation of its ions, because they move with *approximately* the same velocity. If such a salt be present in high concentration upon both or even one side of the interface, its ions will dominate the situation, and, migrating at *nearly* equal velocities, will *tend* to maintain a constant junction-potential difference which undoubtedly is not zero but approaches it within a few millivolts.

Bjerrum (1911) studied the potential differences developed when concentrated solutions of potassium chloride were employed and estimated the theoretical values with the aid of Planck's formula and with the aid of Henderson's formula. He came to the conclusion that the use of a 3.5 M KCl solution would not completely eliminate the potential against hydrochloric acid solutions; but he suggested a more or less empirical extrapolation which would, he thought, give the proper correction. The correction is the difference in the E.M.F.'s of a chain found when first 3.5 M KCl is used and then when 1.75 M KCl is used to connect two electrodes.

An instance of the application of this extrapolation is taken from a paper by Sørensen and Linderstrøm-Lang (1924). The cells used were

I — Pt, H_2 (1 atmos.) | 0.01 N HCl + 0.09 N KCl | 1.75 N KCl |
0.1 N KCl, HgCl | Hg+

II — Pt, H_2 (1 atmos.) | 0.01 N HCl + 0.09 N KCl | 3.5 N KCl |
0.1 N KCl, HgCl | Hg+
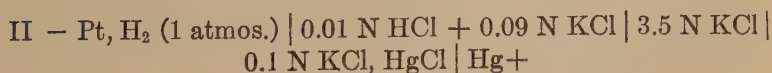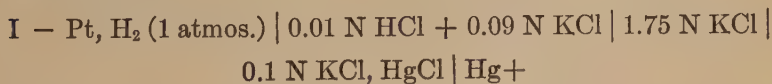
The average potential of cell I at 18° was 0.45688 volt
The average potential of cell II at 18° was 0.45624 volt
The difference was   0.00064 volt

This difference subtracted from the potential of cell II gives $\mathbf{E} = 0.4556$. $\mathbf{E}$ is regarded as the potential of the cell

$$-\text{Pt}, \text{H}_2 \,(1 \text{ atmos.})|0.01 \text{ N HCl}+0.09 \text{ N KCl}\|0.1 \text{ N KCl}, \text{HgCl}\,|\,\text{Hg}+$$
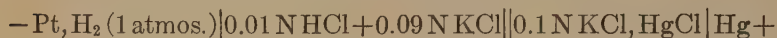
Fales and Vosburgh (1918) made an extensive comparison of various chains, and with the aid of Planck's formula to give the order of magnitude of various contact potentials, and the assumption of equal activities of H^+ and Cl^- ions, they have attempted to assign values which will lead to a general consistency. They concur with others in finding Planck's formula invalid in the assignment of accurate values to liquid junctions, such as:

"xM KCl| 1.0 M HCl and xM KCl| 0.1 M HCl where x ranges from 0.1 to 4.1 and the temperature is 25°C."

They conclude that "there is no contact potential difference at 25° between a saturated solution of potassium chloride (4.1 M) and hydrochloric acid solutions ranging in concentrations from 0.1 molar to 1.0 molar," agreeing with the suggestion of Loomis and Acree (1911).

Because of the great detail concerned in the reasoning of Fales and Vosburgh it is impossible to briefly summarize their work, but before their conclusion can be considered valid it must be noted that they themselves point out that "in an electromotive force combination having a contact potential difference as one of its component electromotive forces, the diffusion across the liquid junction of the one liquid into the other brings about a decrease in the magnitude of the contact potential difference, and this decrease may amount to as much as one-tenth of the initial magnitude of the contact potential difference." This experimental uncertainty undoubtedly renders questionable the *comparability*, if not the precision of measurements by different experimenters. If so there may lurk in the data used by Fales and Vosburgh, in their argument of adjustment to consistency, an indefinite degree of incomparability. The conclusion quoted above is not accepted by all. Consult Aten and van Dalfsen. Scatchard (1925), for instance, follows a method of estimation which leads to the value 0.0047 volt for the potential at the junction

$$\text{HCl } (0.1\text{M}) \,\big\}\, \text{KCl (sat.)}$$
$$\qquad\quad - \qquad +$$
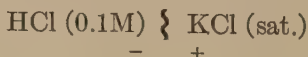
This matter will be discussed at the point where it is shown to affect the standardization of all pH values. See Chapter XXIII.

It has been stated by Sørensen and Linderstrøm-Lang (1924) that in the study of practically all solutions used for biological investigations, with exception of markedly acid or alkaline solutions, the Bjerrum extrapolation gives the same results as the interposition of saturated potassium chloride solution. This is, of course, their direct conclusion from actual measurements and is based on no assumptions. It does not necessarily follow that the liquid junction potential has been eliminated but the approximate identity in the results of the two methods suggests that, even if elimination is not successful, a fairly constant value is involved.

One very pertinent reason for believing that the junction potential between a saturated potassium chloride solution and a buffer solution which is neither very acid or very alkaline is low, is that the concentrations of the excessively mobile hydrogen and hydroxyl ions are negligible. Other things being equal, the junction potential should then be determined largely by such inequality as may exist between the velocities of the potassium and chloride ions. The *tendency* is then *toward* some small, *constant*, liquid-junction potential rather than toward the complete elimination sometimes assumed.

In some of the earlier investigations of liquid junction potentials studies were made with ammonium nitrate. See for instance Abegg and Cumming (1907), Bjerrum (1911), Poma (1914). Drucker (1927) has recently investigated several other salts in bridging solutions. The subject is important to those cases in which a chloride is incompatible with a component of the adjacent solution. See also Aten and Van Dalfsen (1926).

Michaelis and Kakinuma (1923) and Michaelis and Fujita (1923) prefer the employment of potassium chloride in the way indicated below by a type case.

$$\text{Pt, H}_2 \left| \frac{N}{100} \text{ HCl} \right| \frac{N}{100} \text{ HCl + KCl (sat.)} \left| \text{ KCl (sat.), HgCl} \right| \text{Hg}$$

$$\text{A} \qquad \text{B} \qquad\qquad\qquad \text{C} \qquad\qquad\qquad \text{D}$$
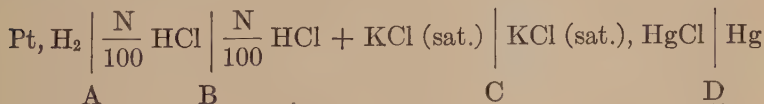
The argument is that since the activities of the hydrochloric acid on the two sides of junction B are nearly the same their

contribution to the junction potential will be low. The junction potential at B will certainly be lower than at

$$\frac{N}{100} \text{ HCl} \,\bigg|\, \text{KCl (sat.)}$$

Likewise the high excess of KCl on both sides of junction C tends to dominate the situation there. Michaelis and Fujita give examples showing that their method yields substantially the same results as the Bjerrum extrapolation.

The argument is not rigid enough for the purposes of Chapter XXIII.

While the Bjerrum extrapolation is still frequently used, its theoretical basis is insecure and its results are unsatisfactory. Therefore, it seems preferable to ignore it. The use of a saturated solution of KCl is preferable since it provides a reduction of contact potential sufficient for many purposes and a simple and widely used procedure, adherence to which makes possible the comparison of "pH *numbers*" as obtained by a uniform procedure. Data obtained with 3.5N KCl are often not comparable with those obtained with saturated KCl as bridging solution.

As indicated by the quotation from Harned (see page 268) no precise solution of the problem can be obtained until some means is found for definitely determining the individual ion activities and transport numbers without involvement of cells having liquid junction potentials. Until a precise solution is found we must be sceptical not only of absolute values sometimes assigned to the potentials at junctions of even simple solutions but guardful of our acceptance of statements regarding the potentials at the junction of complex solutions when the basis of estimation is not precisely given.

CHAPTER XIV

Hydrogen Half-Cells

We can only explore the world with apparatus, which is itself part of the world.—Eddington.

THE BASE OF THE HYDROGEN ELECTRODE

Usually the base of a hydrogen electrode is simply a piece of platinum foil or wire. If wire is used an end is fused into a glass tube and the latter is filled with mercury to form a convenient means of making contact with the lead from the potentiometer circuit. The free end of the platinum wire may then be wound upon a machine screw. On withdrawing the screw the wire is left in a neat coil. If foil is used it may be cut to a very short ⊤ and the stem fused into the glass tube as was the wire; but this is not advisable except when very thin foil is used. Usually the stem is made by welding to the foil a short piece of platinum wire. The welding as follows. *Over* a piece of polished steel, heat the two pieces of platinum to a white heat with a blast lamp. Suddenly strike the hot pieces against the steel with a flat punch. Next, draw off a soft, lead-free glass tube to a *thin* and *blunt* point. Break the capillary tip to permit the wire to enter. Slip the wire in until the foil touches the glass. Then, with foil uppermost, rotate the tube with the junction in the tip of a fine, hot flame. Let the glass fuse until a perfect seal is made and a little of the glass fuses to the edge of the foil. The steps are illustrated in figure 44.
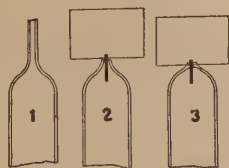
FIG. 44. CONSTRUCTION OF SIMPLE ELECTRODE

It is important to avoid a seal with too thin a glass junction, for such a seal may easily be broken. It is likewise important to avoid too heavy a seal for then proper annealing becomes difficult. A little experience enables one to make seals requiring no special annealing. If a light but substantial junction with the edge of the foil is made the electrode will be rugged.

For highly refined investigations it may be an advantage to make the seal with an alcohol flame and thus avoid the injurious effects upon platinum of the sulfur in ordinary gas. Under no circumstances should there be used a glass (e.g., "Pyrex") having a coefficient of expansion very different from that of platinum, for imperfections of the seal are sure to develop. In this connection it may be said that the most frequent mistake in making electrodes is the use of too large a sealing wire. Large wire is resorted to in order that the pendant foil may be held in place. The inevitable result of the use of so large a wire is that the glass seal becomes subject to imperfections which, while not detected at first, may permit fatal creepage of mercury from the interior junction to the exposed exterior. Some prefer to do away with the mercury within the glass tube. They solder a copper lead to the end of the platinum wire which is destined to be within the glass tube. This, of course, is quite permissible and sometimes advisable if done properly and with design, but the good technician will not humble himself by doing it to avoid creepage of mercury through cracks. Fear of mercury creepage under the very best of conditions, while never disturbing the author, has led some investigators to prefer the all-wire connection.

By the trick of catching the edge of the foil with the softened glass the electrode is stiffened and then the wire leading through the glass seal may be made so small that a good seal is very easily made. Foil 0.08 mm. thick, 1 centimeter square welded to wire 0.08 mm. in diameter does very well.

In place of platinum foil, gauze is sometimes used. Thus Schmidt and Finger (1908) refer to the "Cottrell-electrode" which consists of two cylinders of platinum gauze separated from one another by fusing their rims to rings of glass. A platinum lead welded to each cylinder connects with a separate mercury cup. There are thus formed two electrodes. The advantage of gauze is a large catalytic surface. The disadvantage is that the diffi-

culty of cleaning the crevices will make a careful technician nervous.

It is sometimes assumed that complete equilibrium can be attained only when the hydrogen in the interior of the metal supporting the platinum black is in equilibrium with that on the surface. To reduce the time factor of this soaking-in process it is considered advantageous to use as the supporting metal a very thin film of platinum or iridium deposited upon glass. Doubtless the finest of such films could be deposited by holding the glass tangent to the Crookes' dark space of a vacuum discharge and spattering the metal on from electrodes under 5000 volts difference of potential. The method practiced is to burn the metal on from a volatile solvent. The receipt given by Westhaver (1905) is as follows: 0.3 gram iridium chloride moistened with concentrated HCl is dissolved in 1 cc. absolute alcohol saturated with boric acid. To this is added a mixture of 1 cc. Venetian turpentine and 2 cc. lavender oil. The glass, after being dipped in this solution, is "whipped" with a stroke of the arm to throw off excess liquid and then rotated while drying above an alcohol flame. It is then gradually lowered into the alcohol flame and there heated until the film is first reduced to the mirroring metal and this metal then adheres to the *gently* softened glass. The process should be repeated until a good conducting film is obtained.

Gooch and Burdick (1912) have better success with a viscous mixture of pure chloroplatinic acid and glycerine. This is applied with an asbestos swab to the glass which has previously been heated to a temperature which will instantly volatilize the glycerine. The resulting film is heated until it adheres well to the glass.

Meillère (1920) gives the following recipe. Five-tenths gram dry platinum chloride is triturated with 10 or 15 grams of essence of camomile. The mixture is thinned with about an equal volume of methyl alcohol.

Rheinberg (1923) has a patented process of platinizing glass which is used in producing mirrors. (See Glazebrook, vol. 4.)

Mozolowski and Parnas (1926) use *gilded* glass in their quin-hydrone electrode vessel. They dissolve about 0.1 gram gold chloride in a drop of absolute alcohol and while the solution is cooled they add a drop of lavender oil. A drop of the mixture

is placed on the glass and carefully heated. (See also Eilert (1922).)

If after some practice it is found that even deposits can be formed by one or another of the methods, the next difficulty met is in obtaining good adherence of the film to the glass. This must be done by heating sufficiently but at the same time there must be avoided a fusion of such extent that the continuity of the metallic film will be destroyed. If the glass support is made of a "hard" glass such a fusion will be more easily avoided and at the same time volatilization of impurities in the film will be made easier because of the higher temperature permitted. However, in the selection of such a glass one with a temperature coefficient of expansion approximately equal to the platinum should be selected,—chiefly as a provision for the next step which will now be described.

The chief technical difficulty in the preparation of electrodes with the films described is in establishing the necessary electrical connection. An exposed platinum wire contact destroys the object in using the film. Ordinarily the electrode is made by first coating a bar of glass in the end of which there is sealed a platinum wire and then fusing this bar into the end of a glass tube so that the platinum contact is exposed within the tube where mercury contact may be made. Connection with the film is made by the film of metal that runs through the glass seal. It is less clumsy to seal the wire into the end of a glass tube, break off the wire flush with the glass, coat the tube with the film and then cover the exposed wire with a drop of molten glass.

In place of capping the exposed butt of the wire with glass it might be well to try some of the newer synthetic lacquers.

There is so little advantage in these film-electrodes that they are seldom used.

A scheme which is said to partially accomplish the purpose of a thin film of supporting metal is to cover a platinum support with a gold-plate, gold being relatively impervious to hydrogen. It is doubtful whether this reason has much practical weight. Hammett (1922) thinks it has none. However a gold-plate is of great advantage. It offers a surface upon which deposits of "black" adhere well. It forms a support easily dissolved by electrolysis in hydrochloric acid, thus providing an easy means of

removing old deposits. And the character of the gold deposit gives an additional means of testing the cleanliness of the electrode prior to blackening.

For the gold plating of electrodes the following recipe may be used. Dissolve 0.7 gram gold chloride in 50 cc. water and precipitate the gold with ammonia water, taking care to avoid an excess. Filter, wash and dissolve immediately in a KCN solution consisting of 1.25 grams KCN in 100 cc. water. Boil till the solution is free from ammonia.

PREPARATION FOR DEPOSITING BLACK

One of the essentials for making good deposits is a very high degree of cleanliness of the electrode. In addition to the ordinary methods of cleaning it may be necessary to resort to the use of very fine emery paper to remove those spots which sometimes resist solvents. Alcoholic alkali should be used if the fingers or other source of grease touch the foil. Hammett (1922) uses a water scrubber for the final cleaning. A good test of cleanliness is the evenness with which bubbles of hydrogen escape from the surface during electrolysis in dilute sulfuric acid.

A prerequisite for the good deposition of black is adequate distribution of current. A large electrode may require more than one electrical lead.

In the author's practice no electrode is ever subjected to the blast lamp treatment which others recommend. In the first place this is done at great risk to the glass seal which may resist for a few times but which may develop invisible cracks. In the second place blast lamp treatment does not improve the surface of the platinum and may obviously injure it. If redeposition of "black" under favorable conditions fails to yield a good electrode, experience has shown that it is best to retire the electrode from service without hesitation. It is therefore not good practice to so tie up a particular electrode by sealing it into an expensive ground glass stopper or into the vessel itself that there will be fatal hesitation in rejecting it. On the other hand when such practice becomes advisable for certain research purposes the seal should be made in such a way that it may be broken and the electrode replaced.

DEPOSITION OF "BLACK"

According to the work of earlier investigators and the consensus of opinion among more recent investigators there seems to be no difference under *equilibrium* conditions between coatings of platinum-, iridium- or palladium-black. Of the three, iridium is recommended by Lewis, Brighton and Sebastian because of its higher catalytic activity, and palladium by Clark and Lubs (1916) for use in the study of physiological solutions because of the relative ease with which one deposit may be removed before the deposition of the next in the frequent renewals which are often necessary. Palladium black is easily removed by electrolysis in HCl. Deposits of platinum or iridium may be removed by electrolysis in HCl solution, if they are deposited upon a gold plate. They are difficult to remove if deposited on platinum.

Harned (1926), who says that a thin coating of black is essential, gives the following directions: "Good results were obtained by electrolyzing a solution of chloroplatinic acid containing 0.5 gram of platinum in 100 cc. of solution for one minute with a current density of 0.3 ampere per square centimeter of cathode surface."

The author has used deposits of platinum, iridium and palladium upon platinum, upon gold-plated platinum and upon "rhotanium" alloy. Acidified (HCl) 3 per cent solutions of the chlorides of each metal are used without much attention to the exact strength. The current from a four-volt storage battery is allowed to produce a vigorous evolution of gas. The electrode, after the deposition, is connected to the negative pole of the battery, placed in a dilute sulfuric acid solution and charged with hydrogen. It is required that the bubbles of hydrogen then escaping come off evenly, that the electrode shall have been evenly covered with the deposit in thickness sufficient to cover the glint of polished metal, and that the deposit shall adhere under a vigorous stream of water.

The system used by the author for deposition of "black" is as follows. A row of small vessels, such as weighing bottles about 2 cm. diameter and 5 cm. deep are fitted with electrodes. These electrodes are all attached through binding posts mounted on a wooden rail. These in turn are connected to one pole of a double-pole, double-throw switch. The opposite pole is con-

nected with a flexible lead tipped with platinum. This lead is
used to connect with the electrodes to be treated. The middle
connections of the double-throw switch are connected with a 4-volt
storage battery. The other connections are cross-wired. One of
the vessels is filled with hydrochloric acid made by a one-to-one
dilution of ordinary 37 per cent acid. This is used to dissolve
previous deposits with the aid of electrolysis (switch reversed,
treated electrode +). Another vessel is filled with 10 per cent
sulfuric acid for preliminary direct and counter-electrolysis to
test the cleanliness of the electrode. Another vessel is filled with
the platinum, palladium or iridium chloride solution. When using
palladium so-called reagent palladium is used as + electrode
and this is removed from the solution when not in use. After
deposition of the black the electrode under treatment is quickly
placed under a vigorous stream of water and then electrolyzed
in a another vessel of freshly prepared ten per cent sulfuric acid
until thoroughly charged with hydrogen.

When used with inorganic solutions which undergo no decom-
position electrodes may often be used repeatedly, provided they
are kept clean and *not allowed to dry*. When there is any sign
or suspicion of an electrode becoming clogged, poisoned, worn,
dry or in any way injured, there should be not the slightest hesi-
tation in reblackening or even rejecting it.

For the deposition of platinum black Ellis (1916) uses a solu-
tion of pure chloroplatinic acid containing 1 per cent Pt. He
cautions against the use of the lead acetate which has come down
to us in recipes for the deposition of platinum black upon elec-
trodes for conductivity measurements. For the deposition Ellis
uses a small auxiliary electrode and a current large enough to
liberate gas freely at both electrodes. He continues the deposi-
tion with five-minute reversals of current for two hours and ob-
tains a very thick coating.

Beans and Hammett (1925), compare Hammett (1922), see no
reason for the objection to traces of lead which Ellis emphasizes.
Britton (1925) believes lead increases the efficiency. The author
sees no occasion for its introduction. Hammett (1922) finds that
pure chloroplatinic acid prepared by the method of Wichers
(1921) tends to yield bright deposits in place of the usual black.
The inference is that the usual black owes its nature to the

presence of impurities in commercial preparations of chloro-
platinic acid.

Hammett (1922) says:

"For the deposition of platinum black from a solution of chlorplatinic
acid containing a trace of lead ion, current density and concentration of
chlorplatinic acid are of minor importance, except that with very dilute
solutions stirring becomes necessary. Reversing the direction of the cur-
rent at intervals seems to have little effect, but the current should always
pass in the direction of cathodic polarization for some time at the end of the
process if commutation is used. If the final treatment is anodic the reduc-
tion of the oxidation products formed requires so much time that the elec-
trode is slow in coming to equilibrium."

The above statement reflects the usual opinion that current
density is of minor importance.

For the deposition of iridium Lewis, Brighton and Sebastian
(1917) make the gold or gold-plated electrode the cathode in a
5 per cent solution of iridium chloride. "The best results were
obtained with a very small current running for from twelve to
twenty-four hours. Too large a current gives a deposit which
appears more like platinum black and which is easily rubbed off."

Preferences in regard to the thickness of the "black" deposit
vary widely. For instance Harned (1926), Prideaux (1924) and
the writer (see earlier editions) concur in preferring compara-
tively light coats; while Ellis (1916) Blackadder (1925) and
others either state specifically that they prefer heavy coats or
describe an electrolysis of such duration and current density that
very heavy deposits are sure to occur. In the writer's opinion
it is only the nature of the directly exposed surface that counts
in the ideal electrode and very heavy deposits are potentially
dangerous on account of occlusions, if for no other reason. Of
course there must be some "body" in reserve for as Beans and
Hammett (1925) have shown the catalytically active *smooth*
deposits which they have been able to prepare may soon lose
activity. These same investigators point out that occlusions of
acid from the electrolytic bath may seriously affect the apparent
pH value of very poorly buffered solutions when heavily coated
electrodes are used. For such solutions they recommend a plating
of gold covered by the active deposit of smooth platinum which
they obtain by using very pure chloro platinic acid. For the
preparation of pure Pt, see Wichers (1921).

I use deposits barely sufficient in thickness to obscure the glint of polished metal beneath. Compared with one another in the same solution they will agree within 0.02 millivolt. Andrews reports "sluggish" electrodes or even "the complete failure of electrodes due to too heavy deposits" (of Pd).

According to Hofmann (1922) prolonged charging with hydrogen will lower the ability of an electrode to catalyze the reduction of oxygen. This catalysis proceeds better in acid solution than in alkaline solution and it is enhanced by pretreatment of the electrode with alternate cathode and anode polarization. It is difficult to discuss this proposition adequately for there is a very extensive and highly puzzling literature on the effect of oxygen upon platinum catalysts.

Hammett (1922) says:

"In general the time required for attainment of equilibrium depends upon the efficiency of removal of oxygen; and is more a function of the design of the cell and the rate of hydrogen flow than of the properties of the electrode. Electrodes deteriorate under the influence of hydrogen, becoming much more sensitive to traces of oxygen and finally unusable; but the process is partially reversed by exposure to oxygen. Lack of attention to the complete exclusion of oxygen and the use of aged electrodes may produce no ill results on measurements in acid or neutral range, but every care must be taken when the solution is strongly alkaline."

Andrews (1924) reports a detailed study of electrodes coated with palladium black, noting in particular some of the factors which lead to poor deposits such as solutions too concentrated or too dilute. Andrews' general conclusion was that palladium electrodes are less reliable than platinum and his difficulties are certainly worthy of being regarded as a reason for advocating platinum black in place of palladium black. However, it is important to note that Andrews did not use a cell well suited to the demonstration of single-potential stabilities, and it is also interesting to note the following. Dr. Barnett Cohen has made most of the innumerable hydrogen electrode measurements for the Hygienic Laboratory during the last six years and usually with palladium black electrodes. In running through his records I find among quadruplicate measurements with four vessels run in parallel that there are occasional discrepancies which are crossed out and made the occasion for repetitions of measurements.

His tendency in routine measurements is to accept only measurements agreeing within 0.2 millivolt. He evidently considers as satisfactory quadruplicates those which agree *within* 0.1 millivolt. Very many of his results are such. And this with palladium electrodes used as Andrews uses them—apparently.

Palladium black is said to be attacked by hydrochloric acid and is not recommended for the study of such solutions.

HYDROGEN ELECTRODE VESSELS

So many types of vessel have been published that it is difficult to do justice to the advantages of each. The selection must depend in some instances upon the material to be handled, but in any case there are a few principles which it is hoped will be made clear by a discussion of a few of the more widely used vessels.

The usual method of operation is to partially or wholly immerse the electrode in the solution to be measured and then to bubble hydrogen through the vessel till constant potential is attained. The vessel described by Lewis, Brighton and Sebastian (1917) and illustrated in figure 45 is representative of the general type of vessel used for what may be called the classic mode of operation. The following is the quoted description of this vessel:

Hydrogen from the generator enters at A, and is washed in the bubbler B with the same solution that is contained in the electrode vessel. This efficient bubbling apparatus saturates the gas with water vapor, so that the current of hydrogen may run for a long period of time without changing the composition of the solution in the main vessel. The gas rises from the tip C, saturating and stirring the whole liquid from G to F, and leaves the apparatus through the small trap E, which also contains a small amount of the same solution. The platinum wire attached to the electrode D is sealed by lead glass into the ground glass stopper M. L is a joint made by fusing together the end of the platinum wire and the connecting wire of copper. The surface of the solution stands at the height F so that the iridium electrode is about one-half immersed. The apparatus from F through G, H, I to J is filled with the solution. With the form of construction shown it is an easy matter to fill the tube without leaving any bubbles of air. The reservoir K filled with the same solution serves to rinse out the tube I, J from time to time. The whole apparatus may be mounted upon a transite board, or for the sake of greater mobility, may be held in a clamp, the several parts being rigidly attached to one another to avoid

accidental breakage. The whole is immersed in the thermostat about to
the point L.

The tube J dips into an open tube through which communication is made
to other electrode vessels. This connecting tube may be filled with the
same solution as is contained in the hydrogen electrode vessel or with any
other solution which is desired. All measurements with acids are made
with one of the stopcocks H, I, closed. These stopcocks are not greased
and there is a film of acid in the closed stopcock which suffices to carry the
current during measurement. In order to make sure that no liquid poten-
tial is accidentally established, the second stopcock may be closed up and
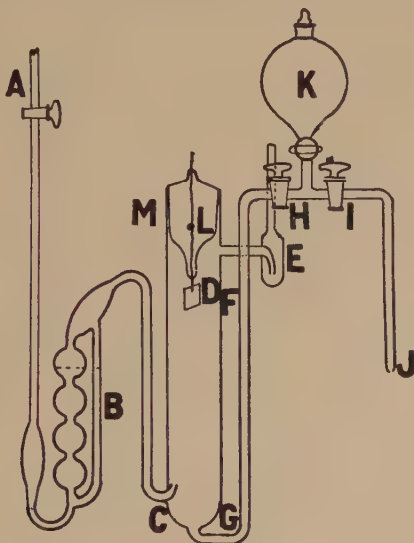
Fig. 45. Hydrogen Electrode Vessel of Lewis, Brighton and
Sebastian

the first opened. No difference of potential in acid solution has ever been
observed during this procedure (but this is not true for solutions of salt
and alkalies). If it is desired that both stopcocks be open, the same liquid
that is in the electrode vessel is placed in the connecting tube at J and
the stopcocks H and I are opened after the current of hydrogen has been
cut off by the stopcock A, and the opening of the trap E has been closed.

If hydrogen enters the cell at the rate of one or two bubbles per minute
several hours are required for the saturation of the solution and for the
removal of air. After this time the potential is absolutely independent of
the rate of flow of hydrogen and the generator may be entirely cut off for
many hours without any change.

Gerke and Geddes (1927) describe a vessel especially designed for the study of cells such as Pt, H_2 | HCl, HgCl | Hg when the electrolyte is very dilute. There are numerous other designs for the special purposes of investigations on the electrochemistry of special cells.

For some biochemical studies such vessels are unsuitable. It is sometimes absolutely essential that equilibrium potentials be established rapidly. The necessity is perfectly apparent when one is dealing with an actively fermenting culture. It is not always so apparent when dealing with other solutions, but it is suspected that absolutely complete equilibrium is never attained in some complex biochemical solutions and that we have to depend upon speeding the approach to equilibrium between hydrogen and hydrogen ions till a virtual equilibrium point is attained (see Chapter XVIII).

It was shown by Michaelis and Rona (1909) that a fairly constant E. M. F. is quickly attained, even in blood, if the platinized electrode, previously saturated with hydrogen, is allowed to merely touch the surface of the solution. This is probably due, as suggested by Hasselbalch (1913) and again by Konikoff (1913), to a rather sharply localized equilibrium at the point of contact. Reductions and gas interchanges having taken place within the small volume at the point of contact, diffusion from the remaining body of the solution is hindered by the density of the surface layer with which alone the electrode comes in contact.

In exploring new fluids it appeared hazardous to the writer to rely upon such a device, which appears to take advantage of only a localized and hence a pseudo-equilibrium, and which makes no allowance for a possible difference between the solution and surface film in the activity of the hydrogen ions. Hasselbalch's (1911) principle seemed therefore to be more suitable.

Hasselbalch found that a very rapid attainment of a constant potential can be obtained by shaking the electrode vessel. Under these conditions there should be not only a more rapid interchange of gas between the solution, the gaseous hydrogen, and the electrode, an interchange whose rapidity Dolezalek (1899) and Bose (1900) consider necessary, but the combined or molecular oxygen, or its equivalent, in the whole solution should be more rapidly brought into contact with the electrode and there

reduced.   Furthermore, by periodically exposing the electrode the hydrogen is required to penetrate only a thin film of liquid before it is absorbed by the platinum black.   The electrode should therefore act more rapidly as a hydrogen carrier.   For these reasons a true equilibrium embracing the whole solution should
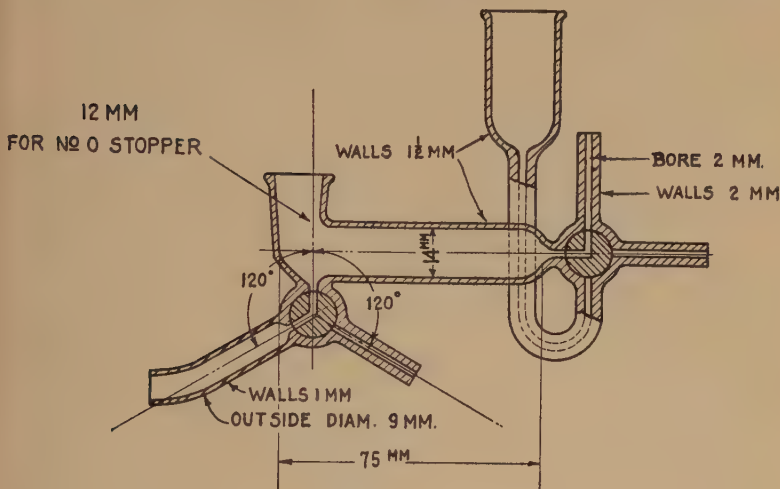
FIG. 46. A HYDROGEN ELECTRODE VESSEL
(Clark (1915).   Drawing by courtesy A. H. Thomas Company)

. *Notes.*   In submitting this working drawing to a glass blower it shall be specified that: (1) Cocks shall be joined to chamber with a neat and wide flare that shall not trap liquid.   (2) Cocks shall be ground to hold high vacuum.   (3) Bores of cock keys shall meet outlets with precision.   (4) The handles of keys shall be marked with colored glass to show positions of bores.   (5) The handles of both keys shall be on the same side (front of drawing).   (6) Vessel shall be carefully annealed.   (7) Opening for no. 0 rubber stopper shall be smooth and shall have standard taper of the standard no. 0 stopper.   (8) Dimensions as given shall be followed as closely as possible.   (9) No chipped keys or violation of the above specifications shall be accepted.

be rapidly obtained with the shaking electrode; and indeed a constant potential is soon reached.

Eggert (1914–1915) in Nernst's laboratory made a study of the rapidity of reduction by hydrogen electrodes in which he compared the effect of alternate immersion and exposure to the hydrogen atmosphere with the effect of continued immersion.   In the

reduction of metal salt solutions such as ferric salts he obtained a much greater velocity of reduction when the electrode was periodically removed from the liquid carrying a thin film of solution to be exposed to the hydrogen. The maximum velocity was proportional to the platinum surface and the time of contact with the gas. It was independent of the number of times per minute the electrode was raised and lowered. As the reaction neared completion the decrease in velocity of reaction became exponential.

Making use of the principles brought out in the preceding discussion and also certain suggestions noted in the chapter on liquid junction potentials Clark (1915) designed a vessel which appears to have found favor for general use. A working drawing of this vessel is shown in figure 46. This drawing shows the type of three-way cock employed by Cullen. Cullen (1922) also has added a small thermometer for use when the vessel is operated without thermostat control. If solutions more viscous than fresh milk are to be used, the bores of the inlet and outlet tubes should be made larger. If only very small quantities of the solution to be tested are available, the dimensions of the vessel may be reduced. In figure 47 is a diagrammatic sketch of the complete system now in use by the author for ordinary work.

The electrode vessel is mounted in a clamp pivoted behind the rubber connection between J and H. This clamp runs in a groove of the eccentric I, the rotation of which rocks the vessel.[1] In the manipulation of the vessel, the purpose is, first, to bring every portion of the solution into intimate contact with the electrode F and the hydrogen atmosphere, to make use of the principle of alternate exposure and immersion of electrode and then, when equilibrium is attained, to draw the solution into contact with concentrated KCl solution and form a wide contact at H in a reproducible manner. The E.M.F. is measured directly after the formation of this liquid junction.

The vessel is first flooded with an abundance of hydrogen by filling the vessel as full as possible with water, displacing this with the hydrogen, and then flushing with successive charges of hydrogen from the backed-up generator. Water or solution is

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[1] Dr. A. B. Hastings rocks the vessel with the aid of an automobile wind shield wiper operating with compressed air.
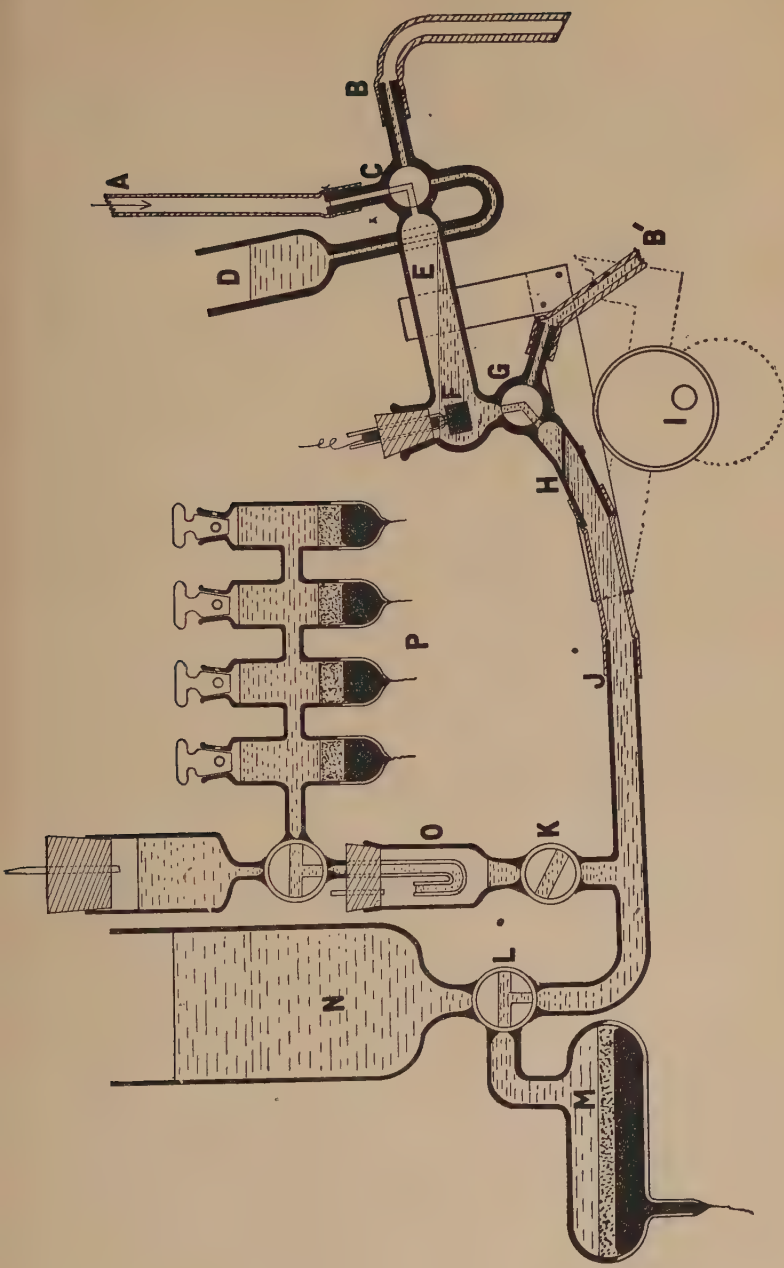
Fig. 47. A System for the Measurement of Hydrogen Electrode Potentials

run into the vessel from the reservoir D which can be emptied through the drain B by the proper turning of the cock C. Solution or hydrogen displaced from the vessel is drained off at B'. These drains when they emerge from the electrical shielding (see p. 357) should hang free of any laboratory drain.

With the vessel rocked back to its lowest position the solution to be tested is run in from D (after a preliminary and thorough rinsing of the vessel with the solution) until the chamber E is about half full. Cock G is closed and cock C is turned so as to permit a constant pressure of hydrogen from A to bear upon the solution. For very careful work it is well to displace dissolved oxygen by first bubbling hydrogen through the solution, provided carbonate solutions are not concerned. The rocking is then commenced and is continued until experience shows that equilibrium is attained with the solution of the type under examination. The eccentric I should give the vessel an excursion which will alternately completely immerse the electrode F and expose it all to the hydrogen atmosphere. The rate of rocking may be adjusted to obtain the maximum mixing effect without churning.

To establish the liquid junction the rubber tube between J and H is pinched while G is turned to allow KCl solution to escape at B'. Then a turn of G and the release of the pinch draws the solution down through the cock to form a broad mixed junction at H. For a new junction the old is flushed away with fresh KCl from the reservoir N by properly setting cock L.

With the closed form of calomel electrode, M, shown in the figure, no closed stopcocks need be interposed between the terminals of the cell. With the customary calomel electrode vessel it is necessary to use a closed cock somewhere and since this must be left ungreased it is well to have it a special cock[2] at J.

If a tube be led out from J and branched, several hydrogen electrode vessels may be joined into the system. In any event it is well to work with two vessels in parallel so that one may be flushing with hydrogen while the other is shaking.

[2] To make an easily turning cock out of which KCl will not creep, grease the narrow part of the socket and the wide part of the key. When the key is replaced there will be two bands of lubricant on which the key will ride with an uncontaminated zone between for the film of KCl solution.

See Shepherd and Ledig (1927) on the preparation of stopcock lubricant.

The electrode F is supported in a sulfur-free rubber stopper. A glass stopper may be ground into place but is seldom of any advantage and may prove to be a mistake. In the first place it is advisable to be free with electrodes and to instantly reject any which fail to receive a proper coating of metal. The inclination to do this is less if it entails the rejection of a carefully ground stopper. Unless the stopper is accurately ground into place it is worthless. Furthermore it is very difficult to so grind a glass stopper that there will be left no capillary space to trap liquid. A rubber stopper can be forced into place without leaving such a space. The rapidity with which measurements are usually taken makes it improbable that a rubber stopper, if made sulfur free, can have any appreciable effect. If the rubber must be protected a coating of paraffin will do.

The calomel electrode M is of the saturated type so that no particular care need be taken to protect it from the saturated KCl used in making junctions. This is the working standard for the accurate standardization of which there is held in reserve the battery of accurately made, tenth-normal, calomel electrodes P. This battery may be connected with the system at any time by making liquid connection at O and opening K.

After a measurement the liquid junction is eliminated, the space rinsed with the tenth normal KCl, and liquid contact *left broken*.

The design of this system is obviously for an air bath. The necessity of raising cocks out of an oil bath would not permit such direct connections as are here shown.

In figure 48 are shown several other designs of electrode vessels. A is one of the original Hasselbalch vessels which has since been modified for the use of replaceable electrodes. B (Sørensen), (Ellis) and C (Walpole), are operated in a manner similar to the vessel shown in figure 45. Walpole's vessel was made of silica and the electrode was of platinum film as described on page 283. D (McClendon and Magoon) was designed for determinations with small quantities of blood. E (Michaelis), employs a stationary hydrogen atmosphere and a wick connection for the liquid junction. See also Farkas (1903) for use of the stationary hydrogen atmosphere. G (Long) is a simple device which the designer thought applied the essential principles of Clark's vessel. Barendrecht's vessel, H, is designed for immersion in an
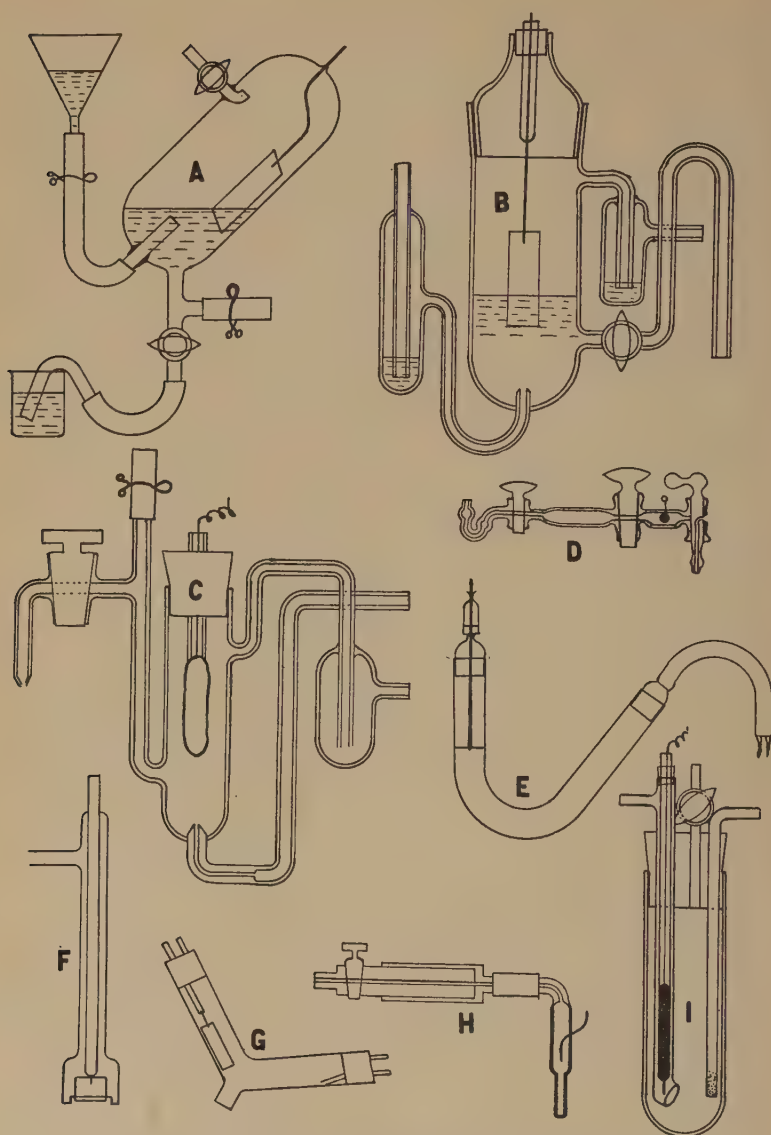
FIG. 48. TYPES OF HYDROGEN ELECTRODE VESSELS

open beaker for estimations during titrations. It is similar to a design of Walpole's (1914), but is provided with a plunger the working of which permits the rinsing of the bulb and the precise adjustment of the level of the liquid. Another immersion electrode is Hildebrand's, F, the successful operation of which depends upon a vigorous stream of hydrogen, which, on escaping from the bell surges the solution about the electrode. It is similar to several simple designs used for a long time in electrometric titrations. A modification which provides better protection of the electrode from oxygen is Bunker's design, I.

Monier-Williams (1924) describes a vessel which is useful for the study of pastes. A straight tube is provided with side tubes for the hydrogen inlet and outlet. The tube is packed with the paste up to the side tubes. At this surface of the paste a wire electrode touches. The other surface of the paste is thrust into a KCl solution.

Vlès and Vellinger (1925) mention the development of the vessel of Vlès, Reiss and Vellinger (1924) for use with plastic materials.

Simms (1923) describes a water-jacketed electrode vessel the water jacket being a local thermostat. See also Rawlings (1926).

In some cases a preliminary reduction of a solution may be accomplished by making the solution, in the presence of hydrogen, travel down a long spiral of platinized wire. The spiral is made by winding no. 24 copper wire closely upon a rod. It is mounted with a spread of the turns just sufficient to hold together descending drops. It is plated with gold and then platinized. Liquid delivered slowly at the top of the spiral will be broken into drops which in the descent of the spiral are thoroughly stirred. The reduced solution is brought into contact with an electrode in a constricted part of the enclosing tube and is then delivered to a continuous-flow liquid junction such as that described by Lamb and Larson or MacInnes (see page 274). The hydrogen by suitable devices may be given the carbon-dioxid partial pressure of the tested solution. Such a scheme is useful only in dealing with continuous treatment processes where abundance of material is available.

Aten and Van Ginneken (1925) in their study of sugar saps of varying pH value used flowing solutions presaturated with hydro-

gen before arrival at the electrode. Their apparatus is described as useful for continuous measurements of flowing solutions.

Keller (1922) has described a hydrogen electrode with a replaceable disk of platinum gauze. This is held by a cap to a hard rubber support which contains a portable calomel electrode. The system is rugged and may be used as an immersion cell for determining the pH values of liquids in commercial processes.

At this point it may be of interest to note that Wilke (1913) attempted to make a hydrogen electrode by using a thin tube of palladium on the interior of which hydrogen was maintained under pressure. One of the difficulties with such an electrode is the estimation of the hydrogen pressure at the solution-electrode interface. Wilke's idea has never been developed to a practical point so far as I know, but it is worthy of study as an immersion electrode for industrial use. See citation to Drucker.

Knobel (1923) describes an electrode which is superficially like Wilke's in that the hydrogen passes from a central core outward to the solution. However Knobel uses a graphite cylinder and it is through the pores of this that the hydrogen makes its way. The outer particles of the graphite are platinized and as the hydrogen passes these it is as if the graphite cylinder were a distributor for the hydrogen which escapes at normal pressure. Schmid (1924) has described some interesting experiments with a similar electrode. Some of Schmid's publications are difficult to obtain but his studies should be watched. They are of considerable interest. For other electrodes see Sannié (1924), Swyngedauw (1927) and particularly the "Birnenelektrode" of Michaelis.

For purposes of titration many of the vessels described for exact measurements, or for special purposes are inconvenient. Therefore there are to be found a number of vessels especially designed for titrations. Hastings' (1921) is one of these. Bovie's (1922) is another.

For titrations and for general utility as well as for potentiometric studies of oxidation-reduction equilibria the vessel with attached calomel half-cell shown in figure 49 has proved useful (See Clark and Cohen, 1923; Studies on oxidation-reduction, III.) The mechanical stirrer shown in their figure is usually not necessary. The holder has been simplified in the design shown by

figure 50. A is a standard "1½ inch pipe lock-nut" the interior
threads of which hold a No. 10 rubber stopper. The interior
diameter of this lock-nut is approximately 4.6 cm. while the
greatest diameter of a No. 10 rubber stopper is about 5 cm.
Therefore the stopper may be ground down at its widest part to
a cylindrical shape of about 4.7 cm. diameter. It is squeezed
into place with the smaller, tapered end projecting and ready to
receive the mouth of a glass cylinder. B is a bar for support.
It is tightly screwed into place. A smaller bar, D, carries the
movable platform E which, when turned into place, supports the
glass cylinder. The calomel half-cell vessel is attached to the
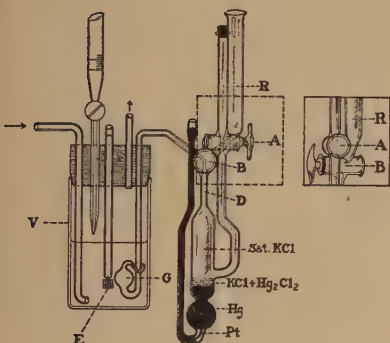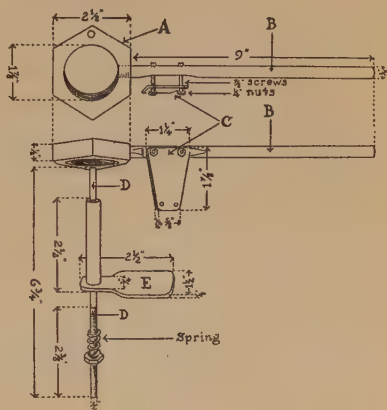
FIG. 49.   FIG. 50.

FIG. 49. ELECTRODE VESSEL WITH ATTACHED CALOMEL HALF-CELL
FIG. 50. HOLDER FOR TITRATION VESSEL AND CALOMEL HALF-CELL

brass plate C by a lead cleat with the bolts shown and a soft copper
wire running through the holes.

The calomel half-cell vessel is shown in figure 49. *Cf.* page 305.

There have recently been several designs of electrode vessel
adapted to operating with very small quantities of fluid. Bodine
and Fink (1925) for instance have cut down dimensions till they
operate with 0.015 to 0.020 cc. of fluid; Bodine (1927) uses 0.01
cc. Their vessel has been employed in studying the blood of
insects and the interior of *Fundulus* egg cells. Winterstein
(1927), also describes a micro vessel.

Lehmann (1923) raises a drop of liquid on a little table in a

tube filled with hydrogen till it makes contact with a platinum point and a capillary liquid junction. The general design has been modified in a number of instances. Solowiew (1926) adapts it to multiple measurements and Radsimowska (1924) to measurements with gels. Wladimiroff and Galwialo (1925) describe difficulties in using the principle with liquids containing CO_2.

Taylor (1925) mentions fine-drawn electrode points designed for micro-injection work. Compare Gelfan (1926).

McClendon (1915) describes a hydrogen-calomel cell of such dimensions that it may be swallowed for measurements of pH in the stomach.

Schaede, Neukirch and Halpert (1921) have an electrode vessel for subcutaneous injection.

In conclusion it may be said that with ordinary care almost any simple combination of electrode and electrode vessel will give fairly good results. On the other hand it is often necessary not only to provide against continuous loss of CO_2 from biological solutions but also to arrange for rapid attainment of equilibrium. Since electrode measurements are often the last resort, since one can easily be misled by pseudo-equilibria and since attention to a few simple details of construction and operation frequently increases very greatly the speed of experimentation, the "simplicity" of certain designs is sometimes more apparent than real.

One of the most astonishing aspects of many of the various designs is the frequency with which there appears no care for the elimination of "dead spaces." There is also an apparent lack of interest in the fact that an equilibrium involving *three phases* has to be established. As Beans and Hammett (1925) have well said the design of a vessel is as important as the nature of the electrode itself in attaining rapidity of measurement. Thus Rice and Rider (1923) describe cases in which as much as 30 minutes were required for the attainment of equilibrium with an ordinary immersion type electrode. This time was very considerably decreased by alternately raising and lowering the electrode, an operation provided for in the use of Clark's vessel.

However it would be invidious to select any particular design for criticism, the more so because none yet published is perfectly adapted to *all* purposes. Those described are therefore to be considered as illustrations from which the reader may select items or suggestions to incorporate in his own design.

"CALOMEL" HALF-CELLS

Unless otherwise specified the calomel half-cell is one in which mercury and calomel are overlaid with a definite concentration of *potassium chloride*. It is commonly called a calomel electrode. For particular purposes some other chloride or hydrochloric acid is used.

The general type of construction is shown by A, figure 51. A layer of very pure mercury is covered with a layer of very pure calomel and over all is a solution having a definite concentration of KCl and saturated with calomel. Calomel, mercurous chloride, is Hg_2Cl_2. For convenience its formula will be written HgCl.[1]

The difference of potential attributed to the interface between mercury and solution is determined primarily by the concentration of the mercurous ions supplied from the calomel. But, since there is equilibrium between the calomel, the mercurous ions and the chloride ions, the concentration of the mercurous ions is determined by the chloride ion activity. This is determined chiefly by the concentration of the KCl. One of three concentrations of KCl is usually employed—either 0.1 molecular, 1.0 molecular or saturated KCl. Half-cells with these concentrations of KCl are ordinarily referred to as the "tenth normal-," "normal-" or "saturated calomel electrodes." These should be distinguished from cells in which the potassium chloride solution is made on the molality basis—number of moles of potassium chloride per 1000 grams of water. 0.1 N KCl is 0.1006 molal and the mercury of the 0.1 N half-cell is 0.00015 volt negative to that of the 0.1 M half-cell.

In figure 51 are shown several calomel electrode vessels each

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[1] Although Ogg (*Z. physik. Chem.*, 1898, 27, 285) showed that the mercurous ion is Hg_2^{++} and accordingly mercurous chloride is often written Hg_2Cl_2, practice has tended to the use of HgCl in describing the calomel half-cell since for usual purposes we are not concerned with this detail.
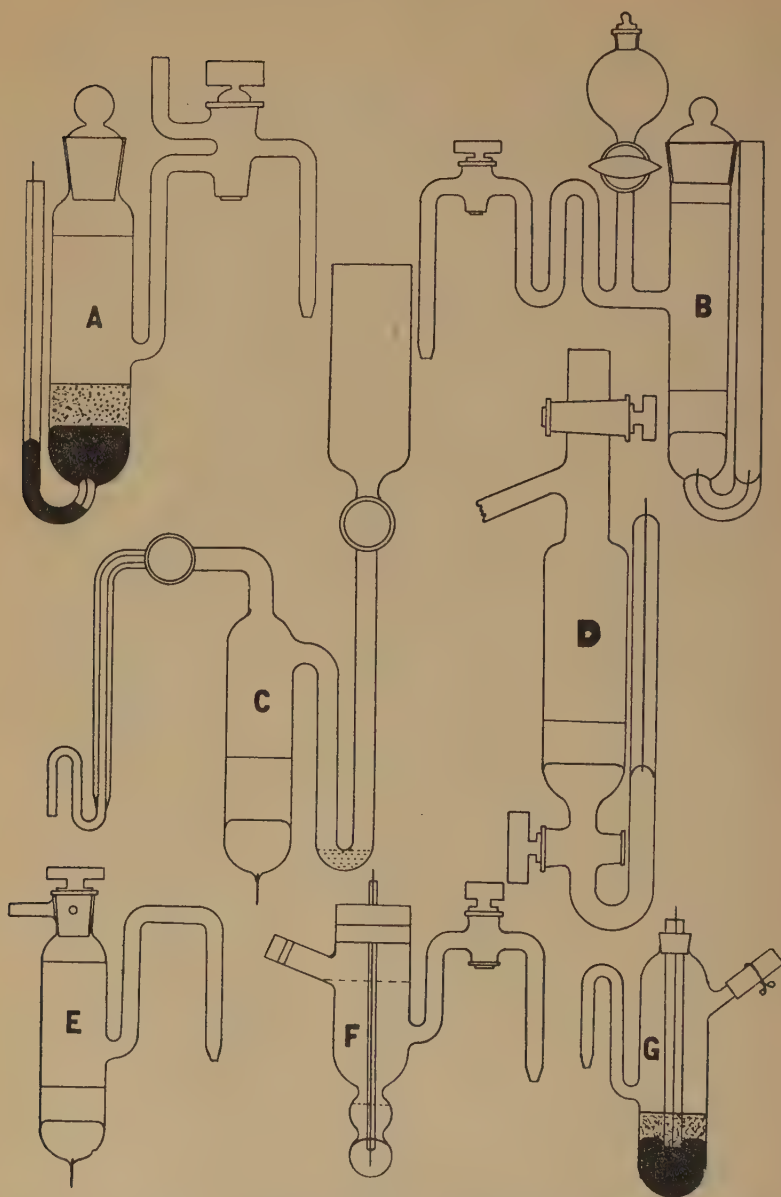
FIG. 51. TYPES OF CALOMEL ELECTRODE VESSELS

with a feature that may be adapted to a particular requirement. Walpole's (1914) vessel, A, is provided with a contact that leads out of the thermostat liquid and with a three-way cock for flushing away contaminated KCl.   A more elaborate provision for the protection of the KCl of the electrode is shown in the vessel of Lewis, Brighton and Sebastian (1917), B.   A form useful as a saturated calomel electrode in titrations is shown at C.   Fresh KCl passes through the U-tube to take the temperature of the bath and to become saturated with calomel shown at the bottom of this U-tube.   D is Ellis' (1916) vessel, which in the particular form shown was designed to be sealed directly to the remainder of the apparatus used.   A valuable feature is the manner of making electrical contact.   Instead of the customary sealed-in platinum wire Ellis uses a mercury column.   On closing the cocks the vessel may be shaken thoroughly to establish equilibrium.   This feature has not been generally practiced.   Vessel E is a simple form useful for the occasional comparison electrode.   It may be made by sealing the cock of an ordinary absorption tube to a test tube and adding the side arm.   F is the vessel of Fales and Vosburgh (1918) with electric contact made as in the familiar Ostwald vessel (G).

In adding new KCl solution to a vessel it must be borne in mind that the solution should be saturated with calomel before equilibrium can be expected.   It is well therefore to have in reserve a quantity of carefully prepared solution saturated with calomel.

In figure 49 is shown a serviceable calomel half-cell which has been used with the attached titration-vessel described on page 301. It is made of Pyrex and therefore the parts are easily joined.   The three-way cock B and the two-way cock A are placed as shown for avoidance of breakage.   Since the platinum contact is made through Pyrex glass the wire should be very fine and the surrounding glass thick.   Wire about 0.06 mm. diameter is used.   The inevitable slight defect of a platinum-Pyrex glass seal is of no consequence in this instance since pure mercury is placed on both sides.   The vessel is filled with cock A open.   Thereafter this cock is kept closed.   Indeed it is feasible to do away with this cock and to draw the tube off to a capillary which is sealed after the filling.   When measurements are being made cock B is turned as shown in the figure.   When not in use the cell is opened to the

reservoir R to accommodate temperature changes. When the liquid junction at G is to be renewed G is flushed from reservoir R. Liquid junction is made at G as follows. The old junction is flushed away by KCl solution from R. Cock B is closed. G is lowered into a portion of the solution to be examined. Through a rubber tube attached to R gentle suction is applied while cock B is cautiously opened. The solution flows gently into G making a sharp junction with the heavy KCl solution. When the junction is at the widest part of G the cock is turned as shown in the figure. It is then assumed that there will be inappreciable diffusion from G through the capillary into the solution to be tested.

This calomel half-cell vessel is attached to the holder of figure 50 by a lead cleat placed at D of figure 49.

In assembling this vessel according to the plan of figure 49 the tube leading from G is broken, run through the rubber stopper and resealed in place.

Usually a calomel half-cell is attached to a reserve of KCl which is not to pass through the half-cell proper but is used to flush liquid junctions.

Some years ago there were demonstrated in exhibits outfits in which this KCl solution for flushing was colored for the convenience of observing liquid junctions. The coloring matter was not revealed. Simms (1923) uses azurine G for this purpose.

PREPARATION OF MATERIALS FOR CALOMEL HALF-CELLS

Mercury

The mercury used in the preparation of these "electrodes" or half-cells should be the purest obtainable. In Chapter XVII methods of purification are described. Sufficient mercury should be used to cover the platinum contact deeply enough to prevent solution reaching this contact on accidental shaking.

More portable half-cells are made by amalgamating a platinum wire or foil. This is done by electrolyzing a solution of mercurous nitrate, the wire being the negative pole. Provision is then made for keeping a paste of calomel about this wire.

Sometimes the platinum wire is amalgamated even when massive mercury is used about it.

Calomel

Some success has been attained with the use of the better grades of calomel supplied on the market but the risk is so great that it is best to prepare this material in the laboratory. A chemical and an electrolytic method will be described.

The chemical preparation of calomel. Carefully redistill the best obtainable grade of nitric acid. Dilute this slightly and with it dissolve some of the mercury prepared as described in Chapter XVII, always maintaining a large excess of mercury. Pour the solution into a large amount of distilled water making sure that the resulting solution is distinctly acid. Now, having distilled pure hydrochloric acid from a 20 per cent solution and taken the middle portion of the distillate, dilute and add it slowly to the mercurous nitrate solution with constant stirring. When the precipitate has collected, decant and treat with repeated quantities of pure distilled water (preferably conductivity water). The calomel is sometimes washed with suction upon a Buchner funnel, but, if due regard be taken for the inefficiency of washing by decantation, it is preferable to wash repeatedly by decantation. There is thereby obtained a more even-grained calomel. Throughout the process there should be present some free mercury.

Electrolytic preparation of calomel. Doubtless the better preparation of calomel is formed by electrolysis according to the method of Lipscomb and Hulett (1916). This is carried out in the same way that the mercurous sulfate for Weston cells is formed. For the preparation of mercurous sulfate Wolff and Waters (1907) employ the apparatus shown in figure 52. An improvised apparatus may be made of a glass tube with paddles, platinum wire electrode and mercury contact and with two spools for bearing and pulley. In place of the sulfuric acid there is used normal hydrochloric acid. Ewing (1925) uses KCl. A direct current (from a four-volt storage battery) must be used. The alternating current sometimes used in the preparation of mercurous sulfate does not seem to work in the preparation of calomel according to some preliminary experiments which Mr. McKelvy and Mr. Shoemaker of the Bureau of Standards kindly made for the writer. During the electrolysis the calomel formed at the mercury surface should be scraped off by the paddles c and c (fig. 52). The calomel formed by this process is heavily laden with finely divided mer-

cury. Indeed it is possible to obtain a finely divided material which consists so largely of mercury itself that, when used in cells subjected to repeated flushing with new potassium chloride solution, the calomel finally becomes washed out. Very good cells are made by combining calomel made by the chemical process
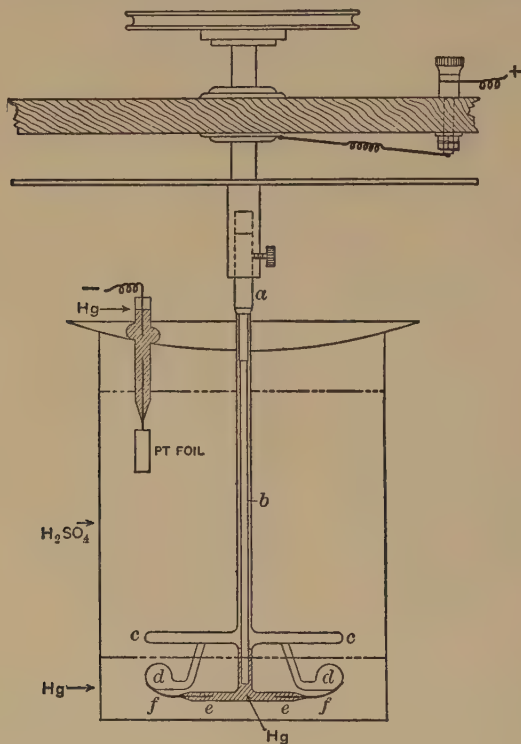
FIG. 52. WOLFF AND WATERS' APPARATUS FOR THE ELECTROLYTIC
PREPARATION OF MERCUROUS SULFATE AS USED FOR THE
PREPARATION OF CALOMEL

and that made by the electrolytic process. The first provides the abundance of calomel; the second the intimate contact with mercury.

Calomel formed by either the chemical or the electrolytic process should be shaken with repeated changes of the KCl solution to be used in the half-cell before the calomel is placed in such a cell.

Potassium chloride

Lewis, Brighton and Sebastian (1917) state that certain grades of commercial KCl are pure enough to be used in the preparation of KCl solutions for the calomel electrode while other samples "contain an unknown impurity which has a surprisingly large effect upon the E.M.F. and which can only be eliminated by several recrystallizations." Gjaldbaek (1924) tells of various so-called "high-grade" commercial preparations which contained various impurities such as ferric salts, ultramarine, etc., evidently from unclean containers. The author has had similar experiences. On one occasion a selenium compound was found! It is therefore obvious that the only safe procedure, in lieu of careful testing by the actual construction of electrodes from different material, is to put the best available KCl through several recrystallizations.

VARIATIONS OF POTENTIAL

The variations in the potentials of calomel electrodes have been the subject of numerous investigations. Richards (1897) ascribed it partly to the formation of mercuric chloride. Compare Richards and Archibald (1902). Sauer (1904) on the other hand concluded that this had little to do with the inconstancy. Arguing upon the well known fact that the solubility of slightly soluble material is influenced by the size of the grains in the solid phase, Sauer thought to try the effect of varying the grain size of the calomel as well as the effect of the presence of finely divided mercury. With cells made up with various combinations he found the following comparisons:

$-$Hg calomel against calomel   Hg$+$ $= 0.00287$ volt
(fine) (coarse)   (fine)   (coarse)
$-$Hg calomel against calomel   Hg$+$ $= 0.00037$ volt
(fine) (coarse)   (coarse) (coarse)
$-$Hg calomel against calomel   Hg$+$ $= 0.0025$ volt
(coarse) (coarse)   (fine)   (coarse)

Lewis and Sargent (1909) state that they do not confirm Sauer in regard to the effect of the finely divided mercury but that they do confirm him in regard to the state of the calomel. These authors and others recommend that grinding the calomel with mercury to form a paste be avoided as this tends to make an un-

even grain.   It is better to shake the mercury and the calomel together but this is unnecessary if electrolytic calomel is used.

In some of the older papers it was suggested that oxygen should be eliminated from the cell.   This has been more or less neglected but recent, highly refined investigations[2] are conducted with the cells deaerated by a stream of pure nitrogen.

By the use of carefully prepared materials and the selection of the better agreeing members of a series, calomel electrodes may be reproduced to agree within 0.1 millivolt or better; but it has not yet been established whether or not this represents the order of agreement among electrodes made in different laboratories. Furthermore there still remains the question of the effect of minor disturbances.   There is no question that "true" values are not to be expected until all parts of the system are in equilibrium and that a preliminary shaking such as Ellis uses will hasten the attainment of equilibrium.   On the other hand a disturbance which will alter the surface structure of the mercury exposed may produce a slight temporary shift in the potential-difference.   The subject remains for systematic investigation.

An extensive investigation of unsaturated calomel electrodes was made by Acree and his students (Myers and Acree, Loomis and Acree), but how far the reproducibility, which they attained by short circuiting the differences of potential, is representative of the general reproducibility of such electrodes is not yet established.

Acree has called attention to the possible concentration of the KCl solution by the evaporation of water and its condensation on the walls of vessels unequally heated in thermostats.

THE "SATURATED" CALOMEL HALF-CELL

This differs in no way from other calomel half-cells except that the solution is saturated with KCl in the presence of solid KCl at all temperatures used.

As a working standard the saturated calomel half-cell is undoubtedly the best as pointed out by Michaelis and Davidoff (1912).   It does not require careful protection from the saturated KCl solution usually employed as a liquid junction and it has a

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[2] See Güntelberg (1926) and Randall and Young (1928) on the action of oxygen on calomel and similar electrodes.

high conductivity permitting full use of the sensitivity of a low-resistance galvanometer.

There is not very good agreement between the values assigned to the saturated[3] calomel half-cell by different laboratories and it had therefore best be regarded for the time being as a good working-standard to be checked from time to time against carefully made normal or tenth normal calomel electrodes or against a hydrogen electrode in a standard solution. For ordinary measurements however the values given in table A of the Appendix are adequate.

VALUES ASSIGNED TO CALOMEL HALF-CELLS

An adequate discussion of the values assigned to calomel half-cells must await the consideration of several matters to be taken up in Chapter XXIII. To clear the way for the difficult presentation of standardization, which is the subject of Chapter XXIII, and to provide a brief review, which may be useful in itself, we may recount here some of the more frequently used values. These values are presented without critical comment. However, the reader should be warned that, quite aside from differences in the ultimate bases of standardization, there is frequently lacking clear definition of what a stated potential refers to. For instance consider the half-cell

$$Hg \mid HgCl, KCl\ (0.1M) \mid KCl\ (sat.) \parallel$$
$$A \qquad\qquad B \qquad\qquad C$$
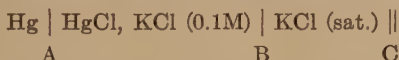
A difference of potential can be allocated to each of the interfaces A and B. At C there is a liquid-junction potential when this half-cell is put in liquid-junction with another half-cell. By means of the symbol $\parallel$ it is in-

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[3] Solubility of KCl in water (The Chemist's Year Book Interpolation of Berkeley's data):

TEMPERATURE	GRAMS KCl PER 100 GRAMS WATER	MOLALITY	TEMPERATURE	GRAMS KCl PER 100 GRAMS WATER	MOLALITY
°C.			°C.		
0	28.13	3.77	40	40.32	5.41
15	32.90	4.41	60	45.88	6.15
20	34.51	4.63	80	50.95	6.83
25	36.00	4.83	100	56.08	7.52
30	37.49	5.03			

Specific gravity of solution saturated at 0° = 1.15 (Seidell's Solubility Tables). Hence solution is about 3.39 N.

Specific gravity of solution saturated at 15° = 1.172. Hence solution is about 3.89 N.

Specific gravity of solution saturated at 25° = 1.1785. Hence solution is about 4.18 N.

dicated that this junction-potential is to be treated separately and that consideration of it is to be neglected in evaluating the potential of the half-cell. Then there remains the potential differences at A and C. When a value for the calomel cell is stated it sometimes means definitely the potential at A, it sometimes means definitely the algebraic sum of the potentials at A and B. Frequently the distinction is not preserved. But more frequently the potential at C, stated to have been taken care of separately, enters the final evaluation of what is really the sum of the potentials at A and B although stated to be the value at A. We shall not attempt to preserve the important distinction until the matter is again discussed in Chapter XXIII.

Largely upon the basis of Palmaer's (1907) work the value 0.560 volt has been used as the "absolute" difference of potential between mercury and N/1 KCl saturated with calomel in the presence of solid calomel at 18°C. (The mercury being positive to the solution.) There is some skepticism[4] regarding the reliability of this value, but for the particular purpose with which we are now concerned it makes little difference what the value is if proper *relative* relations are maintained.

Because of this it has been agreed that some one half-cell shall be made the standard of reference. The hypothetical normal hydrogen electrode has been agreed upon as a standard of reference and potentials of calomel half-cells are usually referred to that standard as having zero potential difference.

In the report of the "Potential Commission" of the Bunsen-Gesellschaft (Abegg, Auerbach and Luther, 1911) the normal hydrogen electrode standard of difference of potential was adopted. The differences of potential between the normal hydrogen electrode and the tenth-normal and normal KCl calomel electrodes were given as 0.337 and 0.284–0.283 respectively. Auerbach (1912) in a review of this report called attention to the smaller temperature coefficient of the potential difference at the tenth-normal calomel electrode when referred to the normal hydrogen electrode (as having zero potential difference at all temperatures) and suggested that the tenth-normal electrode be taken as the working standard with the value 0.3370 between 20°C. and 30°C.

Loomis and Acree (1911) present a choice of values for the tenth-normal calomel electrode at 25°C. referred to the normal hydrogen electrode. The choice depends upon the ionization ascribed to the hydrochloric acid solutions used in their hydrogen electrodes and upon the values of the contact differences of potential which were involved. Loomis (1915) is inclined to accept the value 0.3360.

Clark and Lubs (1916) give a compilation of Bjerrum's values and those of Sørensen and Koefoed published by Sørensen (1912). See table 52.

In 1914 Lewis and Randall applied "corrected degrees of dissociation" to the hydrochloric acid solutions used in arriving at the difference of

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[4] Whether this is just or unjust is a question concerning which we are in doubt. No critical review in the light of modern researches is known to the author.

potential at 25° between calomel electrodes and the theoretical normal hydrogen electrode. Defining the normal calomel electrode as the combination Hg, Hg_2Cl_2, KCl (1M), KCl (0.1M) they reach the value 0.2776. The difference of potential between this electrode and the tenth normal they give as 0.0530. Whence the value for the tenth normal electrode is 0.3306. These values were revised by Lewis, Brighton and Sebastian (1917) to 0.2828 for the difference of potential between the normal calomel and the normal hydrogen electrodes, and 0.0529 for the difference between the normal and the tenth normal. They were revised again by Lewis and Randall (1923) to 0.2822 for the normal cell.

Beattie (1920) calculated for the potential difference at the normal calomel electrode 0.2826 and compares this value with 0.2824 which is Lewis,

TABLE 52

Potentials of "0.1 N calomel half-cell"

AUTHOR	TEMPERATURE	POTENTIAL DIFFERENCE BETWEEN NORMAL HYDROGEN ELECTRODE AND N/10 CALOMEL ELECTRODE WHEN HYDROGEN PRESSURE IS	
		One atmosphere less vapor pressure	One atmosphere
	°C.	*volts*	*volts*
Bjerrum............................	0	0.3366	0.3367
Sørensen and Koefoed ....{	18	0.3377	0.3380
	20	0.3375	0.3378
Bjerrum...........................	25	0.3367	0.3371
Sørensen and Koefoed............{	30	0.3364	0.3370
	40	0.3349	0.3359
	50	0.3326	0.3344
	60	0.3290	0.3321
	75	0.3243	0.3315

Brighton and Sebastian's result (see above) when corrected by Beattie for the liquid junction potential difference between 0.1 N and 1 N KCl. For later values see Chapter XXIII and appendix table A.

Michaelis (1914) gives in table 53 several values for the potential differences referred to the normal hydrogen electrode for the tenth normal and the saturated calomel electrodes. See table 53.

Fales and Mudge seem not to have made any independent measurements which furnish more reliable values for the difference of potential between a saturated calomel half-cell and the "normal hydrogen electrode." These authors have however extended the work of Michaelis and have found

evidence that the saturated calomel half-cell is reliable within the temperature interval 5°–60 °C.

Sørensen and Linderstrøm-Lang (1924) are of the opinion that the saturated potassium chloride calomel half-cell, "which offers certain advantages as a working electrode is hardly suitable as a standard." In their study of calomel half-cells with solutions of potassium chloride more concentrated than normal they used 3.5 N KCl. They cite a number of investigations, chiefly in Danish laboratories, of the difference of potential between this half-cell and the tenth normal half-cell at 18° and give 0.0831 as the best value. This is the value of Gjaldbaek (1924).

TABLE 53

Potentials of tenth normal and saturated calomel half-cells

(After Michaelis (1914))

TEMPERATURE	TENTH NORMAL	SATURATED
15		0.2525
16		0.2517
17		0.2509
18	0.3377	0.2503
19		0.2495
20	0.3375	0.2488
21		0.2482
22		0.2475
23		0.2468
24		0.2463
25		0.2458
30	0.3364	
37		0.2355
38	0.3355	0.2350
40	0.3349	
50	0.3326	
60	0.3290	

TEMPERATURE COEFFICIENTS

We have no concern for the temperature coefficient of the absolute potential difference at the calomel electrode. By agreement the potential assigned is that of the cell

$$Hg \mid HgCl, KCl \left\| \begin{array}{c} H^+ \\ a = 1 \end{array} \right| Pt, H_2 \text{ (1 atmos.)}$$
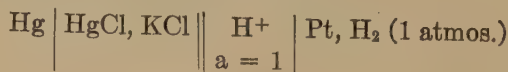
when the potential difference at the normal hydrogen electrode is assumed to be zero *at all temperatures.*

Thus it comes about that the absolute temperature coefficient for the saturated calomel half-cell (as measured directly in absence of thermal equilibrium) is low and positive while by the standard of reference it is high and negative.

There exists in the literature considerable confusion in regard to this matter. Its further discussion will be postponed to Chapters XXII and XXIII, since the question of temperature coefficients is of importance to the subject as a whole.

THE SILVER CHLORIDE ELECTRODE

Comparable in principle to the so-called calomel electrode is the half-cell: Ag|AgCl, definite chloride solution. This is frequently called the silver chloride electrode. It may be used as a standard half-cell just as the mercury-calomel-KCl half-cell is used; but it has been put to use chiefly in theoretical studies on the activities of chlorides in solution.

Linhart (1919) prepared his silver as follows: "the silver was deposited by a current of 5 to 7 amperes in a cell consisting of an anode of silver and a cathode of fine platinum wire, dipping into a solution of silver nitrate. Under the influence of this large current the silver gathered about the platinum wire in loose, spongy clots easily loosened by a slight tapping of the wire. The silver so obtained was then washed and kept under pure water until needed."

Güntelberg (1926) confirms American workers in finding that silver formed from cyanide solutions gives a more negative potential than those samples which are deposited from silver nitrate solutions, from the reduction of silver nitrate with ferrous sulfate (Brønsted) or by heating Ag_2O (Lewis). He used a spiral of platinum covered with Ag_2O, converted the latter to silver at 500° and then deposited AgCl by electrolysis. He keeps oxygen out by use of pure nitrogen and surrounds the electrode with AgCl *crystals* made by the slow removal of ammonia (over sulfuric acid) from ammoniacal silver solutions.

MacInnes and Beattie (1920) find it advisable to deposit the silver chloride from a solution of the same composition and concentration as that to be used as electrolyte.

They formed a thick deposit of silver on 1.5 cm. sq. platinum gauze by electrolysis (3 milliamperes, 24 hours) in potassium silver cyanide. After washing the electrode they deposited a coating of

silver chloride by 20 minutes electrolysis with 5 to 7 milliamperes in lithium chloride solution.

Scatchard (1925) gives 0.0453 at 25°C for the potential of the cell

$-$ Hg | HgCl, KCl (sat.) $\}$KCl (0.1 Molal), AgCl | Ag $+$ and 0.0466 at 25°C. for the potential of the cell

$-$ Ag | AgCl, KCl (0.1 Molal) | KCl (0.1 Molal), HgCl | Hg $+$

For details concerning this half-cell see: Brønsted (1920), Gerke (1922), Güntelberg (1926), Jahn (1900), Lewis (1906), Linhart (1919), MacInnes and Beattie (1920), MacInnes and Parker (1915), Noyes and Ellis (1917), Scatchard (1925), Sheppard and Elliott (1920), and Randall and Young (1928).

THE MERCURY-MERCURIC OXIDE ELECTRODE

This has played its part in the examination of alkaline solutions. See Chapter XX.

MISCELLANEOUS STANDARD HALF-CELLS

As described in Chapter X a hydrogen electrode half-cell with a solution of known hydrogen ion concentration is useful. Such half-cells require no further mention here. However it may be noted that Pinkhof (1919) suggested special half-cells with single potentials equal to those of a hydrogen electrode at selected end-points of titrations. Sharp and MacDougall (1922) describe lead and cadmium electrodes having such potentials for the range pH 4 to pH 10. Such devices are of little use except for standardized procedures of extensive routine. Then they may be very useful.

In addition there are the innumerable electrodes of general electro-chemistry. References to the older literature will be found assembled by Abegg, Auerbach and Luther (1911–1915). Lewis and Randall in *Thermodynamics* have discussed several standard half-cells which may be adapted to special purposes in the construction of cells one half-cell of which is to be the hydrogen half-cell.

Of very great usefulness is the quinhydrone electrode in standardized solution. See Chapter XIX.

CHAPTER XVI

THE POTENTIOMETER, NULL-POINT INSTRUMENTS AND ACCESSORY EQUIPMENT

An excellent example of an actual process which is very nearly reversible is furnished when the electromotive force of a galvanic battery is measured by means of a sensitive potentiometer.—LEWIS AND RANDALL.

With the newest galvanometers you can very well observe currents which would require to last a century before decomposing one milligram of water.—HELMHOLTZ (in 1881).

We ordinarily speak of measuring the electromotive force of a cell in a casual manner as if it were merely the measurement of a potential difference. However, it is perfectly well known that if the cell is allowed to furnish current it will "run down" and ultimately will furnish no electromotive force. To allow the cell to furnish current during the measurement is obviously to take the measurement with declining potential. Likewise the cell, if reversible, will act as an accumulator when current is fed to it. To put the matter more elegantly we may say that the measurement must be made under conditions of reversibility and maximum work (see Chapter XI). Therefore, instead of applying directly some instrument such as a volt-meter, which draws current, we nicely balance the electromotive force of the cell by an opposing, external electromotive force. No current passes through the cell at such a balance. This lack of current is made evident by absence of effect in an indicating instrument, the null-point instrument.

This is the Poggendorf compensation method, the potentiometer method. In a sense the null-point instrument, for example, a galvanometer, serves two purposes; that of an indicator in the potentiometric method itself, and that of an indicator of the fact that so far as the electrical phenomena themselves are concerned the cell is operating close to that infinitesimal rate which is one condition of maximum work.

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THE POTENTIOMETER

The principle of the potentiometer may be illustrated by the arrangement shown in figure 53 which is suitable for very rough measurements.

According to elementary modern theory the flow of electricity in metals is the flow of electrons, the electron being the unit electrical charge. By an unfortunate chance the two kinds of electricity, which were recognized when a glass rod was rubbed with silk, were given signs (+ for the glass and − for the silk) which now leave us in the predicament of habitually speaking of the flow of positive electricity when the evidence is for the flow
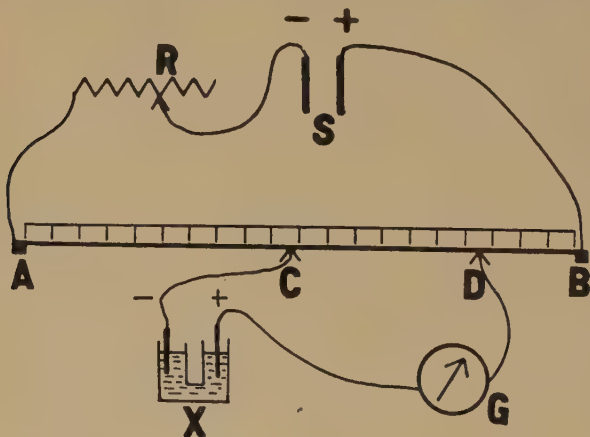
FIG. 53. ELEMENTARY POTENTIOMETER

of negative charges, the electrons. But so far as the illustration of principles is concerned it makes little difference and we shall depart from custom and shall deal with the negative charges in order to make free use of a helpful but very incomplete analogy. We may imagine the electrons, already free in the metal of our electrical conductors, to be comparable with the molecules of a gas which if left to themselves will distribute themselves uniformly throughout their container (the connected metallic parts of our circuits). We may now imagine the battery S (fig. 53) as a pump maintaining a flow of gas (electrons) through pipes (wires) to R to A to B and back to S. The pipe (wire) AB

offers a uniform resistance to the flow so that there is a uniform fall of pressure (potential) from A to B while the pump (battery) S maintains a uniform flow of gas (electrons). If we lead in at C and D the ends of the pipes (wires) from another pump (battery) X, taking care that the high pressure pipe (wire) from X leads in on the high pressure side of AB, we can move C, D or both C and D until they span a length of AB such that the difference of pressure (difference of potential) between C and D on AB is equal and opposite to the difference of pressure (difference of potential) exerted between C and D by X. Then no current can flow from X through the current-indicating instrument G and we thereby know that balance is attained.

If we know the fall of electrical potential per unit length along AB the difference of potential exerted by X will be known from the length of wire between C and D. We now come to the manner in which this fall of potential per unit length is determined.

Choosing for units of electrical difference of potential, electrical resistance and electrical current, the volt, the ohm, and the ampere respectively, we find that they are related by Ohm's law:

$$\text{Current (in amperes)} = \frac{\text{Difference in potential (in volts)}}{\text{Resistance (in ohms)}}$$

or

$$C = \frac{E}{R} \tag{1}$$

With this relation we could establish the fall of potential along AB by measuring the resistance of AB and the current flowing. But this is unnecessary, for we have in the Weston cell a standard of electromotive force (E.M.F.) which may be directly applied in the following manner. The unknown X (figure 53) is switched out of circuit and in its place is put a Weston cell of known E.M.F. Adjustment of C and D is made until the "null-point" is attained, when the potential difference between the new positions of C and D is equal to the E.M.F. of the Weston cell. From such a setting the potential fall per unit length of AB is calculated. It must be especially noted however that for such a procedure to be valid the current in the potentiometer circuit must be kept *constant between the operations of standardization and of measure-*

ment for the fundamental relationship upon which reliance is placed is that of Ohm's law, $C = \dfrac{E}{R}$.

It will be noted that the establishment of the difference of potential between any two points on AB by the action of S and the resistance of AB is strictly dependent upon the relation given by Ohm's law; but, since we draw no current from X when balance is attained, the resistance of *its* circuit is of no fundamental importance. It only affects the current which can flow through the
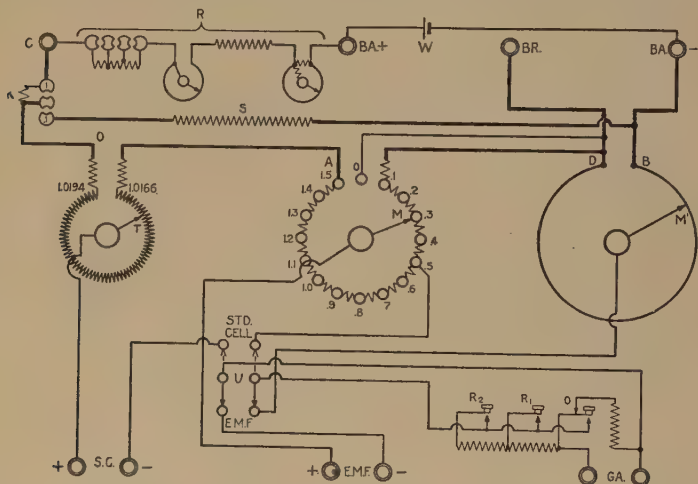
Fig. 54. Wiring of the Leeds and Northrup Potentiometer (Type K)
(Courtesy of Leeds and Northrup Company)

indicating instrument G when the potential differences are out of balance. It is therefore concerned only in the sensitivity of G.

The simple potentiometer system described above is susceptible to refinement both in precision and in convenience of operation.

With the inevitable variations in the potentiometer current which occur as the battery runs down it would be necessary to recalculate from moment to moment the difference of potential per unit length of the wire AB if the procedure so far described were used. This trouble is at once eliminated if the contacts of the Weston cell can be thrown in at fixed points and the current be then adjusted by means of the rheostat R so that there is

always *the same* uniform current producing, through the resistance between the Weston cell contacts, the potential difference of this standard cell. Having thus arranged for the adjustment of a uniform current at all times and having the resistance of AB already fixed it is now permissible to calibrate the wire AB in terms of volts.

In the Leeds and Northrup potentiometer (fig. 54), the resistance AB of the elementary instrument (fig. 53) is divided into two sections one of which A–D (fig. 54) is made up of a series of resistance coils between which M makes contact and the other portion of which is a resistance wire along which M′ can slide.
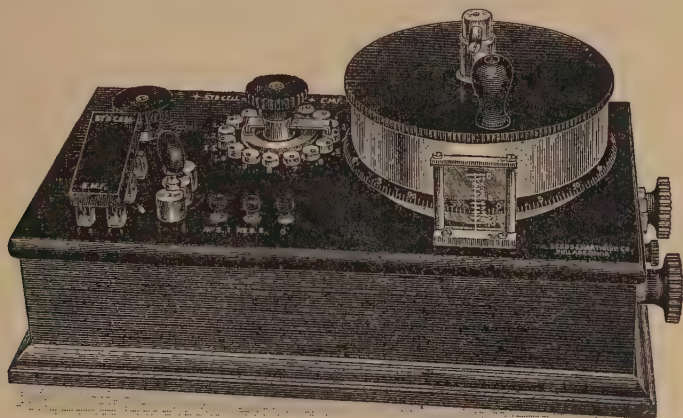
FIG. 55. THE LEEDS AND NORTHRUP POTENTIOMETER
(Courtesy of Leeds and Northrup Company)

When the potentiometer current has been given the proper value, in the manner which will be described, the fall of potential across any one of the coils is 0.1 volt so that as M is shifted from the zero point 0 the potential difference between M and D is increased 0.1 volt at each step. Likewise, when the current is in adjustment, the shifting of M′ away from D increases by infinitesimal[1] fractions of a volt the difference of potential between M and M′.

To adjust the potentiometer *current* so that the several re-

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[1] There is, of course, a limit, an indefinite limit, to the divisions readable. There is also a limit below which a reading would have no meaning if the errors of calibration were neglected.

sistances in the potentiometer circuit will produce the differences of potential in terms of which the instrument is calibrated, use is made of the Weston cell in the following manner.   By means of a switch, U, the unknown is thrown out and the Weston cell is thrown into circuit.   One pole of the Weston cell circuit is fixed permanently.   The other can be moved along a resistance at T, constructed so that the dial indicates the value of the particular cell in use.   When so placed as to correspond with the value of the Weston cell in use this contact at T is left in its position.   Now the current flowing from the battery W is adjusted by means of the rheostat R until the difference of poten-
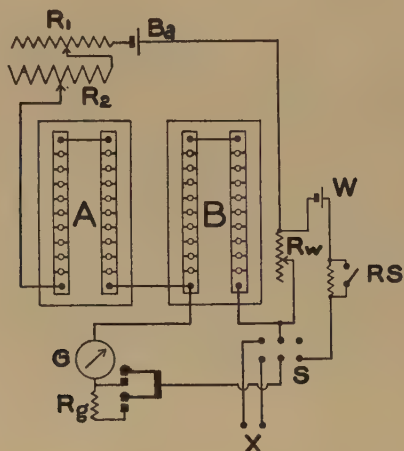
FIG. 56. ARRANGEMENT OF "RESISTANCE BOXES" FOR POTENTIOMETER

tial between T and 0.5 balances the potential difference of the Weston cell as indicated by the cessation of current in the galvanometer GA.   The resistance T to 0.5 is such that the E.M.F. of the battery acting across this resistance will produce the desired potentiometer current.   This current now acting across the several resistances furnishes the indicated potentials, i.e., a potential difference of 0.1 volt across each coil.

Another arrangement which employs the ordinary sets of resistances in common use is illustrated in figure 56.

A and B are duplicate sets of resistances placed in series with the battery Ba and adjusting rheostats R_1 and R_2.   If the cur-

rent be kept uniform throughout this system the potential difference across the terminals of B can be varied in accordance with Ohm's law by plugging in or out resistance in B. But to keep the current constant, while the resistance in B is changed, a like resistance is added to the circuit at A when it is removed from B, and removed from A when it is added to B.

As mentioned before, the potential difference could be determined from the resistance in B and a measurement of the current; but this is avoided by the direct application of a Weston cell of known potential. Assuming *constant current*, a Weston cell, W, replaces X by adjustment of switch S. Adjustment to the null-point is made by altering the resistance in B with compensation in A. The unknown is then thrown into circuit and adjustment of resistance made to the null-point by changing A and B. If E_w is the known E.M.F. of the Weston cell, E_x the potential of the measured cell, r_w the resistance in circuit when the Weston cell is in balance and r_0 the resistance in circuit when the measured cell is in balance we have

$$C \text{ (constant)} = \frac{E_x}{r_0} = \frac{E_w}{r_w}$$

Whence

$$E_x = E_w \frac{r_0}{r_w} \tag{2}$$

The system is improved by providing rheostats R_1 and R_2 to regulate the potentiometer current till constant difference of potential is attained between terminals. Then the resistances may be calibrated in volts.

It is further improved by introducing resistance R_w, placed as is the exterior resistance T of figure 54, and Weston cell at W.

It will be noted that in this arrangement every one of the plug contacts is *in the potentiometer circuit*. A bad contact, such as may be produced by failure to seat a plug firmly during the plugging in and out of resistance, or by corrosion of a plug or dial contact, will therefore seriously affect the accuracy of this potentiometer system. It requires constant care.

Lewis, Brighton and Sebastian (1917) used two decade resist-

ance boxes of 9999 ohms each. With an external resistance the current was adjusted to exactly 0.0001 ampere. Thus each ohm indicated by the resistance boxes when balance was attained corresponded to 0.0001 volt. Their standard cell which gave at 25° 1.0181 volts was spanned across B (fig. 56) and 182 ohms of the external resistance, R_w.

Another mode of using the simple system illustrated in figure 53 is a device frequently used by physicists, and introduced into hydrogen electrode work by Sand (1911) and again by Hildebrand (1913). Instead of calibrating unit lengths along AD by means of the Weston cell, or otherwise applying the Weston cell directly in the system, the contacts C and D carry the terminals of a voltmeter. When balance is attained this voltmeter shows directly the difference of potential between C and D, and therefore the E.M.F. of X.[2]

A diagram of such an arrangement is shown in figure 57. There is an apparent advantage in the fact that the Weston cell may be dispensed with and resistance values need not be known. There are however serious limitations to the precision of a voltmeter and, in two cases which the author knows, accuracy within the limited precision of the instruments was attained only after recalibration.

A voltmeter is generally calibrated for potential differences imposed at the terminals of leads supplied with the instrument.

Turning again to figure 53 we recall that when any given fall of potential occurs between A and B, a definite current flows in the circuit SRAB. If the resistance of AB is known, a measure of the current flowing permits one to calculate the fall of potential between A and B. Thus a current-measuring instrument (ammeter) placed in series with the fixed resistance AB may be

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[2] It is sometimes assumed that because the circuit of the system under measurement is placed in the *position* of a shunt on the potentiometer circuit that its resistance must be high in order that CD (fig. 53) may indicate correctly the potential difference. The fact that no current flows in this branch when balance obtains shows clearly that its resistance can have no effect on the accuracy of the indication. It has also been assumed that if CD is spanned by a voltmeter, the resistance of the voltmeter should be taken into consideration. But a voltmeter is *calibrated* to always indicate the potential difference between *its terminals*, which should be considered part of the instrument itself.

calibrated to indicate differences of potential between A and B.
To use this system the terminals of the cell C and D (fig. 53)
are moved to A and B and there permanently fixed. An am-
meter is placed between R and S and adjustment of R is made
until no current flows in G. The difference of potential between
A and B, as indicated by the calibrated and renamed reading of
the ammeter, is then equal to the E.M.F. of the gas chain.

Much the same limitations noted in the voltmeter system apply
to the ammeter system.
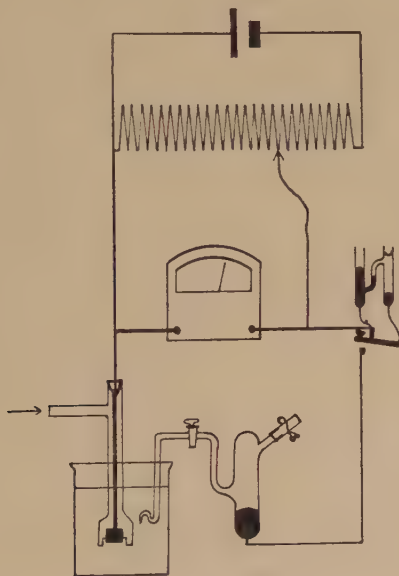
FIG. 57. VOLTMETER POTENTIOMETER SYSTEM

A modification of the system briefly described above is found
in the "Pyrovolter." The essential modification is a device of
wiring whereby the same indicating instrument is used to measure
current (indicated in volts) and to indicate the null-point.

Of potentiometer characteristics little need be said for the
choice in the first instance will lie between instruments sold by
reliable makers. In the second instance the choice will lie be-
tween instruments of different range and many of the unique

instruments may be at once eliminated by a calculation which shows that the reputed accuracy involves too close a scale reading to be reliable. Certain difficulties which enter into the construction of potentiometers for accurate thermo-couple work are hardly significant for the order of accuracy required of hydrogen electrode work. The range from zero to 1.2 volts and the subdivisions 0.0001 volt do for measurements of ordinary range and accuracy. There should be a variable resistance to accommodate the variations in individual Weston cells of from 1.0175 to 1.0194 volts, and provision for quickly and easily interchanging Weston cells with measured E.M.F.

Several of the features of standard potentiometers may be eliminated to reduce their cost without injury to their use for hydrogen electrode measurements. Steps in this direction have been taken by at least one manufacturer.

Having described the fundamental principles of the potentiometer it seems hardly worth while to discuss the numerous modifications found among manufactured instruments or used in the construction of home-made designs. With the advent into every town of the numerous and varied parts of radio apparatus certain accessory parts of a potentiometer may be readily purchased and the amateur can concentrate his attention upon the essential resistances. But, unless he is equipped to make these with accuracy and to mount them with care, he may waste the cost of a satisfactory instrument.

With regard to the more special or unique designs found on the market it may simply be said that they were developed for special purposes and that unless these special purposes are to be accommodated, the purchaser will do well to depend only upon an instrument of universal applicability.

When rubber is used as the insulating material of instruments employed as potentiometers the rubber should not be left exposed to the light unduly. The action of the light not only injures the appearance of the rubber but also may cause the formation of conducting surface layers.

If the potentiometer system contains a sliding contact and this contact is *not* involved in the resistance of the primary potentiometer circuit proper, the contact should be kept heavily coated with pure vaseline. If there be any doubt whatever about the

quality of this vaseline it should be boiled with several changes of distilled water, skimmed off when cool and then thoroughly dried. If this is done there will seldom be any need to resort to the heroic and dangerous procedure of polishing.

It cannot be too strongly emphasized that while a low order of precision is often adequate for a certain purpose the employment of crude measuring instruments often obscures the data of greatest significance. This statement should not be interpreted as a discouragement to those who are about to undertake measurements with some such system as that illustrated in figure 57
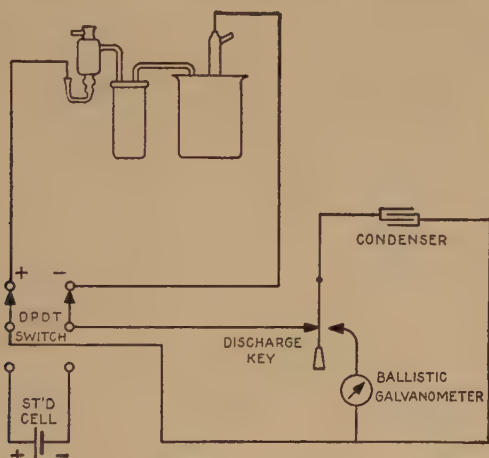
FIG. 58. DIAGRAM OF CONNECTIONS FOR CONDENSER METHOD OF MEASURING POTENTIAL DIFFERENCES

(Courtesy of Leeds and Northrup Company)

for important data have been obtained with just such instruments. The statement is intended rather as an encouragement to the beginner who will find the handling of more precise instruments easy and the rewards rich.

BALLISTIC GALVANOMETER SYSTEM

In a few instances there has been employed a system of measurement, the principle of which is illustrated in the wiring diagram of figure 58. See Beans and Oakes (1920). The E.M.F. of a cell is allowed to charge a fixed condenser. By throwing

the discharge key to the right the charge accumulated by the condenser is allowed to discharge through a ballistic galvanometer, the deflection in which may be made a measure of the accumulated charge and hence of the E.M.F. of the cell.

The ballistic galvanometer is one designed to indicate by the angular deflection of its coil the quantity of electricity passing through the coil as a sudden discharge. The quantity of electricity stored in the condenser is a function of its dimensions and material and of the difference of potential imposed at its terminals. The dimensions and material being fixed, the charge becomes proportional to the difference of potential. A definite difference of potential may be imposed by means of the Weston cell. The resulting charge in the condenser is discharged through the ballistic galvanometer giving the coil a definite deflection. This serves to calibrate a given set-up if the galvanometer is so designed that the deflection at each section of the scale is proportional to the quantity of electricity discharged through the coil and if the wiring be such that no serious changes of capacity and inductance occur in manipulation.

The advantage of this condenser method is that the condenser may be conveniently made of such capacity that insignificant current is drawn from the cell under measurement. If, then, the technique used at the electrodes is refined, it should be possible to measure equilibrium potentials which would be easily displaced by current withdrawal. However, until there are published more definite data relating the conditions of electrode measurements to the theory of the condenser method, this system is not to be recommended for ordinary use.

USES OF THE ELECTRON TUBE

The 3-electrode thermionic vaccum tube has been used in several arrangements for following changes in the electromotive forces of cells.

The tube referred to is one or another of the several tubes used as detectors or amplifiers in radio communication. A glass tube (figure 59 (1)), exhausted to a very low gas pressure is supplied with an atmosphere of electrons by their emission from the hot filament F. These electrons produce what may be called a space charge in the tube. Surrounding the filament is a metallic sheath

called the plate, P.   If this is maintained by the battery B at a
potential positive to the filament, the electrons will migrate to
the plate and there is established a unidirectional current known
as the plate current.   Interposed between filament and plate is
a grid, G, of wire or perforated sheet metal, through which the
electrons must pass in their migration from filament to plate.
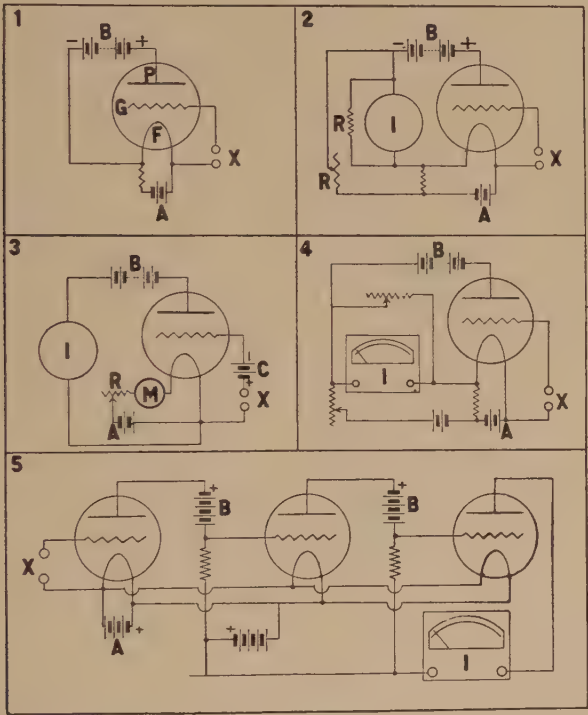
FIG. 59. WIRING DIAGRAMS FOR ELECTRON VALVE "POTENTIOMETERS"

If this grid be charged positively with relation to the filament
it will aid in the withdrawal of electrons from the filament; but
if this grid be charged negatively with relation to the filament it
will oppose the electron emission.   In figure 60 there is shown
by the curve marked 0 the plate current at different plate
voltages when the grid is not charged.   For such a relation the
filament must be maintained with constant current.   If a posi-

tive potential of 4.5 volts is placed on the grid, the plate current, with change of plate potential, follows the indicated curve of figure 60. Now choose constant plate voltage, e.g., 40 volts and see the second chart of figure 60. The plate current is now revealed as a function of grid potential. If the filament current were now increased the curve would be shifted. If the plate current is to be nearly a linear function of grid potential, the plate potential, filament current and the grid potential itself must be adjusted till the operation is within the straighter portion of such a curve.

Goode in his first article gives the relation between grid potential and grid current shown in figure 60 for the particular tube and
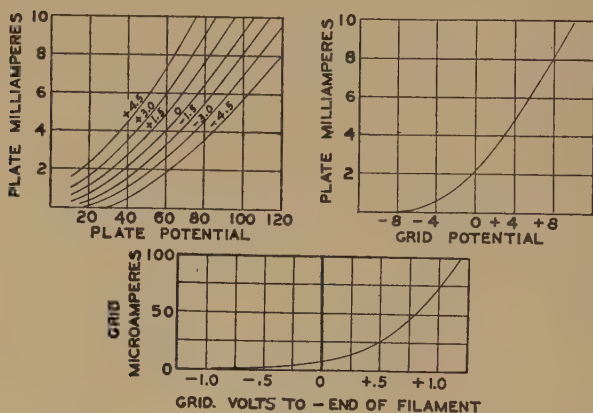
Fig. 60

working condition he used. He notes that, unless the grid be given a negative potential, enough current may be drawn to discharge a hydrogen electrode. He, therefore, connected the hydrogen electrode terminal to the grid and the calomel electrode terminal to the negative end of the filament. Others use a "C" battery to make the grid more negative. This should not be overdone, for slight currents in the opposite direction may be produced in the grid circuit as the grid is made more negative.

Goode (1922) applies the principle in the device shown by figure 59 (2). The cell was placed at X. A galvanometer, I, was used as the plate current indicating instrument. Since the sensitivity of the galvanometer was too high its terminals were shunted by

resistances, R. A calibration curve was then plotted from gal-
vanometer deflections at known potentials of X.   Goode obtained
good titration curves with this device. He emphasized the ad-
vantages of the principle to be: first, continuous reading without
the balancing for each potential required in the potentiometer
system; second, the possibility of such a design that no, or at
most very little, current is drawn from the cell.

Goode called attention to the fact that steady operation re-
quires steady filament current. Williams and Whitenach (1927)
introduce a rheostat R and ammeter M (see figure 59 (3)), to
aid in this control. By reference to figure 60 it will be observed
that the plate current declines as the grid potential becomes more
negative. By use of a "C" battery (Figure 59 (3)) Williams and
Whitenach were able to operate with the galvanometer un-
shunted. Bienfait (1926) (see figure 59 (4)) introduces as a
current indicating instrument a millivolt meter, I, of 300 ohms
and scale range of 17 millivolts. The compensation current and
value per scale division on this reading instrument are regulated
by rheostats.

Goode (1925) elaborated upon his original design by that
shown in figure 59 (5). However, he has recently replaced this
(personal communication) with a two valve system, which he has
so wired that the indicating current shown by a milliammeter
of 15 milliampere range is very closely proportional to the po-
tential difference between filament and grid produced by the cell
under measurement.

It is sometimes stated that the use of the electron valve in-
volves no withdrawal of current from the cell under measure-
ment. Whether this is true or not in the specific case depends
upon the characteristics of the particular tube in use and how
they are utilized but particularly upon the negativity of the grid
with relation to the filament. Goode in a private communica-
tion cites evidence that he can produce conditions under which
no appreciable current is drawn.

Since the operation of a tube depends upon its characteristics
which may change, upon filament current, which may change,
upon "B" battery potential, which may change, calibration of
the relations between indicating current and grid-filament poten-
tial difference is necessary not only in the first instance but at

intervals thereafter. For descriptions of the detail in the management of tubes see Van der Bijl (1920).

For other wiring diagrams and applications of the electron valve to cell measurements see: Calhane and Cushing (1923), King (1924), Treadwell (1925), Wendt (1927), Pope and Gowlett (1927), Buytendyk, Brinkman and Mook (1927), Buytendyk and Brinkman (1927), and Voegtlin and De Eds (1928).

There are various possible extensions of the electron valve to the purposes of hydrion control as in the control of mechanical devices, etc.

NULL-POINT INSTRUMENTS

Referring to figure 53 and the accompanying text the reader will see that in the balancing of potential differences by the Poggendorf compensation method there is required a current indicating instrument to determine the null-point. Such instruments will be briefly described, and some of their characteristics discussed.

In the selection of instruments for the measurement of the electromotive force of cells it is desirable that there should be a balancing of instrumental characteristics and the selection of those best adapted to the order of accuracy required. A null-point instrument of low sensitivity may annul the value of a well-designed, expensive and accurate potentiometer; and a galvanometer of excessive sensitivity may be very disconcerting to use. The potentiometer system and the null-point instrument should be adapted one to the other and to their relation to the system to be measured.

The several corrections which have to be found and applied to accurate measurements of hydrogen electrode potentials are matters of a millivolt or two and fractions thereof. Collectively they may amount to a value of the order of 5 millivolts. Whether or not such corrections are to be taken into account is a question the answer to which may be considered to determine whether a rough measuring system or an accurate one is to be used. For all "rough" measurements the capillary electrometer is a good null-point instrument. It has a sufficiently high resistance to hinder the displacement of electrode equilibria at unbalance of a crude potentiometer system. It is easily constructed by anyone with

a knowledge of the elements of glass blowing, and without particular care may be made sensitive to 0.001 volt.

For "accurate" measurements there is little use in making an elaborate capillary electrometer or in temporizing with poor galvanometers.

The apportionment of galvanometer characteristics is a complicated affair which must be left in the hands of instrument makers, but there are certain relations which should be fulfilled by an instrument to be used for the purpose at hand, and general knowledge of these is quite necessary in selecting instruments from the wide and often confusing variety on the market.

THE GALVANOMETER

The galvanometer is a current-indicating instrument, which, in the form useful for the purpose at hand, consists of a coil of wire suspended in the magnetic field of a strong permanent magnet. The leads to the terminals of this coil are the upper and lower "suspensions." They are connected to the circuit in which the presence of current is to be detected. If current flow through the coil, it will produce a magnetic field. This, interacting with the field of the permanent magnet, causes the coil to turn till it tends to embrace the maximum number of lines of force. Obviously the approach to the maximum is determined largely by the torsion of the suspensions.

Provision should be made for mounting a galvanometer where it will receive the least vibration. If the building is subjected to troublesome vibrations some sort of rubber support may be interposed between the galvanometer mounting and the wall bracket or suspension. Three tennis balls held in place by depressions in a block of wood on which the galvanometer is placed may help. In some instances the more elaborate Julius suspension, such as those advertised, may be necessary. It is certainly a great help and, for extensive work, quite worth the trouble and expense of installation.

Complete formulation of galvanometer conduct is an extremely complicated problem, including as it does the properties of materials. We shall pass a discussion of this and come at once to the end result,—the description of a galvanometer in terms of its sensitivity, as determined experimentally.

GALVANOMETER SENSITIVITY

Galvanometer sensitivities are expressed in various ways. Since one's attention is centered upon detecting potential differences the temptation is to ask for the galvanometer sensitivity in terms of microvolt sensitivity. There are two ways of expressing this which lead to different values. One is the deflection caused by a microvolt acting at the terminals of the galvanometer.
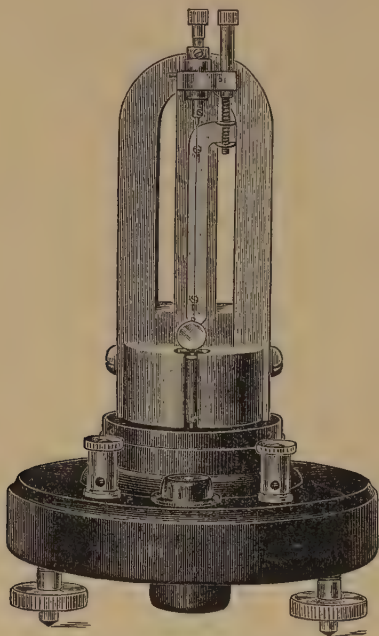
FIG. 61. A GALVANOMETER
(Courtesy of Leeds and Northrup Company)

The more useful value is the deflection caused by a microvolt acting through the external critical damping resistance. But in the last analysis the instrument is to be used for the detection of very small *currents* and these currents when allowed to flow through the galvanometer by the unbalancing of the circuit at a slight potential difference are determined by the total resistance of the circuit. The instrument might be such that a microvolt at the terminals would cause a wide deflection, while, if forced

to act through a large external resistance, this microvolt would leave the galvanometer "dead." For this reason it is best to know the sensitivity in terms of the *resistance* through which a unit voltage will cause a given deflection. This is the megohm sensitivity and is defined as "the number of megohms (million ohms) of resistance which must be placed in the galvanometer circuit in order that from an impressed E.M.F. of one volt there shall result a deflection of one millimeter" upon a scale one meter from the reflecting mirror (Leeds and Northrup catalogue 20, 1918). The numerical value of this megohm sensitivity also represents the microampere sensitivity if this is defined as the number of millimeters deflection caused by one microampere.

In hydrogen electrode measurements the resistance of the cells varies greatly with design (length and width of liquid conductors) and with the composition of the solutions used (e.g. saturated or M/10 KCl). Constricted, long tubes may raise the resistance of a chain so high as to annul the sensitivity of a galvanometer unless this has a high megohm sensitivity.

In the practical attainment of a given sensitivity we enter complexities, since the arrangements by which high megohm sensitivity is attained affect other galvanometer characteristics. One of these, which is not essential but is desirable, is a short period. A short period facilitates the setting of a potentiometer. If the circuits are out of balance, as they generally are at the beginning of a measurement, the direction for readjustment may be inferred from the direction of galvanometer deflection without bringing the coil back each time to zero setting, but there comes a time when prompt return to zero setting is essential to make sure that slight resettings of the potentiometer are being made in the proper direction.

DAMPING

For a return of the coil to zero without oscillation it is necessary to have some sort of *damping*. This is generally a shunt across the galvanometer terminals, the so-called critical damping resistance. This shunt permits a flow of current (when the main galvanometer circuit is opened) which is generated by the turning of the coil in the magnetic field. The magnetic field produced in the coil by this current interacting with the field of the perma-

nent magnet tends to oppose the further swing of the coil.   When
the resistance of the shunt is so adjusted to the galvanometer
characteristics that the swing progresses without undue delay to
zero setting and there stops without oscillation, the galvanometer
is said to be *critically damped*.   Critical damping as applied to
deflection on a closed circuit need not be considered when the
galvanometer is used as a null-point instrument.   Since some of
the best galvanometers are not supplied with a damping resist-
ance the purchaser of an outfit for hydrogen electrode work should
take care to see that he includes the proper unit.   Underdamped
and overdamped instruments will prove very troublesome or
useless.

If there is no damping, the coil will oscillate like a free, torsion
pendulum.   If infinitely damped, the coil would never return to
zero setting.   If underdamped, the coil will oscillate but will
come to rest rapidly.   If overdamped, the coil will not oscillate
but will come to rest too slowly.

These very brief considerations are presented merely as an aid
in the selection of instruments.   The manner in which desirable
qualities are combined is a matter of considerable complexity but
fortunately makers are coming to appreciate the very simple but
important requirements for hydrogen electrode work and are
prepared to furnish them.   A galvanometer used by the author
had the following characteristics; coil resistance 530 ohms, critical
damping resistance 9,000 ohms, period 6 seconds, sensitivity 2245
megohms.   It was not the ideal instrument for the hydrogen
electrode system in use but was very satisfactory.   A shorter
period is desirable and a higher coil resistance to correspond
better with the average resistance of the order of one to two
thousand ohms in some gas chains, would be desirable; but im-
provement in both of these directions at the same time may in-
crease the expense of the instrument beyond the practical worth.
Indeed certain instruments now on the market are satisfactory
for almost any type of hydrogen electrode measurements.

In using a galvanometer it is important to remember that while
the E.M.F. of a cell is unbalanced its circuit should be left closed
only long enough to show the *direction* of the galvanometer deflec-
tion.   Otherwise current will flow in one direction or the other
through the chain and tend to upset the electrode equilibrium.

A mere tap on the key which closes the galvanometer circuit is sufficient till balance is obtained.

CAPILLARY ELECTROMETER

The capillary electrometer depends for its action upon the alteration of surface tension between mercury and sulfuric acid with alteration of the potential difference at the interface. A simple form suitable for that degree of precision which does not call for the advantages of a galvanometer is illustrated in figure 62.

Platinum contacts are sealed into two test tubes and the tubes are joined as illustrated by means of a capillary K of about 0.5 mm.
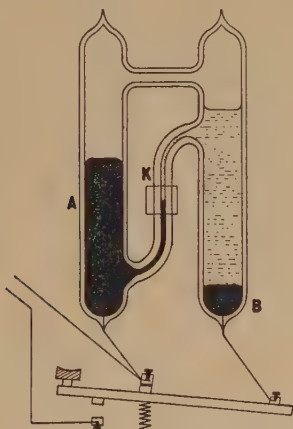
FIG. 62. DIAGRAM OF CAPILLARY ELECTROMETER AND KEY

diameter. In making the seals between capillary and tubes the capillary is first blown out at each end and can then be treated as a tube of ordinary dimensions in making a T joint. After a thorough cleaning the instrument is filled as illustrated with clean, distilled mercury, sufficient mercury being poured into the left tube to bring the meniscus in the capillary near a convenient point. In the other tube is now placed a solution of sulfuric acid made by adding 5.8 cc. water to 10 cc. sulfuric acid of 1.84 specific gravity. The air is forced out of the capillary with mercury until a sharp contact between mercury and acid occurs in the capillary. The instrument is now mounted before a microscope

using as high power lenses as the radius of the glass capillary will permit. The definition of the mercury meniscus is brought out by cementing to the capillary with Canada balsam a cover glass as illustrated.

Mislowitzer (1928) projects the image of the mercury meniscus upon a screen and thereby obtains high magnification.

Among the numerous other forms of capillary electrometer there might be mentioned that of Müller (1926). He uses the double capillary effect, that is the rise at the one end and the fall at the other end of a thread of mercury. He claims that the double effect can be satisfactorily followed with a reading glass.

Bennett (1925) uses, in his two-capillary instrument, tubes of 0.012 mm. diameter. He finds that smaller tubes are apt to exhibit a "sticking effect" while of course larger tubes decrease the sensitivity. The 1925 edition of "Ostwald-Luther" states that tubes at least 0.3 mm. wide should be employed.

Menzel and Krüger (1926) use a tube 0.8 mm. diameter. They use $2N$ H_2SO_4 (not the concentration of highest conductivity) and recommend capillaries of uniform round bore.

An important feature in the use of the capillary electrometer is its short circuiting between measurements. This is done by the key shown in figure 62. Tapping down on the key breaks the short-circuit and brings the terminals of the electrometer into the circuit to be balanced. If the E.M.F. is out of balance the potential difference at the mercury-acid interface causes the mercury to rise or fall in the capillary. Releasing the key short-circuits the terminals and allows the mercury to return to its normal position. Adjustment of the potentiometer is continued till no movement of the mercury can be detected. To establish a point of reference from which to judge the movement of the mercury meniscus the microscope should contain the familiar micrometer disk at the diaphragm of the eye piece. In lieu of this an extremely fine drawn thread of glass or a spider web may be held at the diaphragm of the eye piece by touches of Canada balsam.

THE QUADRANT ELECTROMETER

The quadrant electrometer has not been very frequently used as a null-point instrument in potentiometric measurements but

it will come into more frequent use with the development of the "glass electrode" and the study of non-aqueous solutions of low conductivity (see Hall and Conant, 1928). Bovie uses it in general.

In a form useful for the purpose at hand a very light vane of aluminium is suspended by an extremely fine thread, preferably of quartz, which is metallized on the surface in order to conduct charges to the vane. The vane or "needle" is surrounded by a flat, cylindrical metal box cut into quadrants each highly insulated. Two opposite quadrants are connected to one terminal and the remaining quadrants to another terminal. If now the vane or needle be charged from one terminal of a high-voltage battery the other terminal of which is grounded, and a difference of potential be established between the two sets of quadrants, the needle will be deflected by the electrostatic forces imposed and induced.

Since the current drawn for its operation is only the amount necessary to charge a system of very low capacity to the low potential difference when the potentiometer is slightly out of balance with the measured E.M.F. (and to zero potential difference at balance) the quadrant electrometer might be of special value in the study of easily displaced, electrode equilibria. However, the attainment of the desired sensitivity with some of these instruments is a task requiring skill and patience. Furthermore the rated sensitivity is sometimes attained by adjusting the so-called electrostatic control to such a value that the zero position of the needle is rendered highly unstable. This, combined with the very long period at high sensitivity, renders the instrument unsatisfactory for common use. Against these objections are: first, the point mentioned above, and second the advantage that the instrument may ordinarily be left in circuit during the adjustment of the potentiometer as is not the case with the galvanometer.

For discussions of "electrostatic control" see for instance Beattie (1910–1912) and Compton and Compton (1919).

The quadrant electrometer is especially useful in the study of "glass electrodes" (see page 432). In the circuit of the glass electrode the resistance may be of the order of "over fifty megohms." Therefore the ordinary current-indicating instru-

ments, such as the galvanometer, suffer great impairments of sensitivity. A static instrument must replace them.

A wiring diagram for a quadrant electrometer is shown in figure 63. R_1 is a resistance of about 2 megohms, interposed merely to prevent high discharge currents on accidental short-circuit of the high potential battery B. The double-throw switch S_1 provides for grounding the electrometer needle during adjustments. By means of switch S_2 the quadrants may be grounded during adjustments, or the one pair of quadrants may be connected to one pole of the cell X which is under measurement. The other pole of X is connected to the other pair of quadrants and the potentiometer grounded at O. Kerridge (1926) prefers to lead the connections from each pair of quadrants to a switch that permits the position of the quadrant pairs in the wiring to be
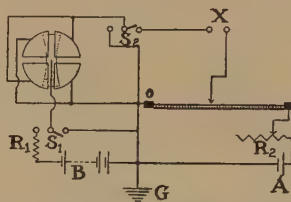
FIG. 63. WIRING DIAGRAM OF POTENTIOMETER SYSTEM IN WHICH A QUAD-
RANT ELECTROMETER IS USED AS NULL-POINT INSTRUMENT

reversed. The potentiometer circuit is shown in elementary outline with the potentiometer battery A, regulating rheostat R_2 and grounding, G, at the zero end, 0. For a discussion of shielding and insulation see Chapter XVII, and Brown (1924).

Kerridge (1926) also describes the use of the "Lindemann electrometer." See Lindemann and Keeley (1924).

TELEPHONE RECEIVER

The modern high resistance telephone receiver of the type used in radio reception may serve in an emergency [Kiplinger (1921)]. Lack of balance between potentiometer adjustment and measured E.M.F. is indicated by a click in the receiver when the potentiometer key is tapped; but there is of course nothing but the loudness of the click to show how far from balance the adjustment

is, and only the decrement of the sound to indicate that adjustment in the proper direction is being made.

There are those who prefer potentiometer, null-point instrument and electrode vessel mounted together. In consequence there are on the market a wide variety of so-called portable sets. Several of these are described in the literature. The author prefers to give each part of a set its appropriate mounting according to the needs of the investigation.
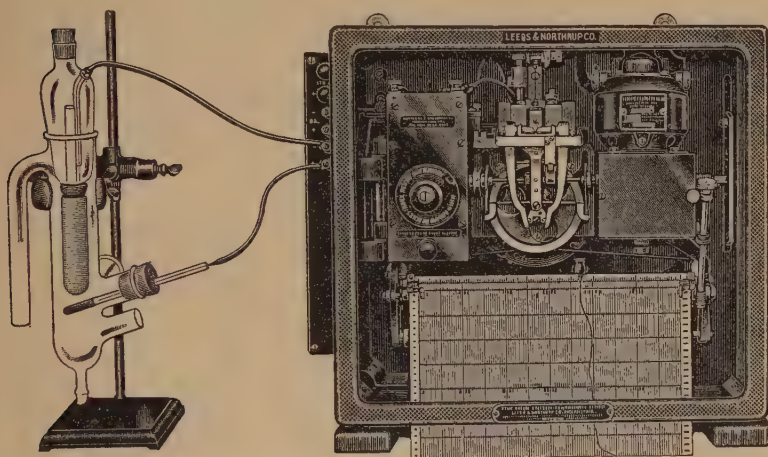
FIG. 64. LEEDS AND NORTHRUP RECORDING POTENTIOMETER
(Courtesy of Leeds and Northrup Company)

RECORDING POTENTIOMETERS

For recording potential changes within the range of the extended wire of the Leeds and Northrup potentiometer, Gesell and Hertzmann (1926) attach a spindle to the drum, wind a thread about this and run the end of this thread to the writing point of a kymograph.

An automatic recording potentiometer is manufactured by the Leeds and Northrup Co. The shaft which rotates the potentiometer wire also holds an adjustable disk with knobs for contact with a relay circuit. At a determined potential a relay can

be actuated and through this control various mechanical apparatus can be operated.

Numerous photographic devices are available for recording galvanometer deflections. Buytendyk, Brinkman and Mook (1927) used photographic records with the electron valve system.

THE WESTON STANDARD CELL

Among several cells which give fairly constant, determined electromotive forces, the Weston cell is the one most frequently used. Indeed it has become an international standard for the practical maintenance of the value of the international volt.

The elementary construction of the Weston cell is illustrated in figure 65. Pure mercury forms one electrode and a cadmium
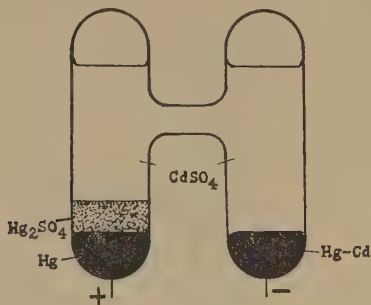
FIG. 65. DIAGRAM OF THE WESTON STANDARD CELL

amalgam the other. The mercury electrode is overlaid with mercurous sulfate. The electrolyte solution is a solution of cadmium sulfate. Two chief forms of the cell are in use. In one the cadmium sulfate solution is maintained at the saturation point by the presence of solid cadmium sulfate not shown in the diagram but present on each side. In the other cell, referred to as the "unsaturated" cell, in contradistinction to the "saturated" cell, the concentration of cadmium sulfate in solution is that of a solution saturated at 4°C. This results in a solution which is unsaturated at ordinary temperature.

It is the saturated cell, sometimes called the normal cell, that is used to maintain the value of the volt, since it is regarded as the more reproducible and constant. On the other hand the unsaturated cell is often preferred for routine use because it is easily

made portable and because it has a temperature coefficient so small as to be negligible for many purposes.

Electrode potential measurements, made by the ordinary potentiometric method, are referred to the electromotive force of a particular Weston cell or set of Weston cells. Reliability in this basic device is therefore fundamental. Since preparation of reliable cells has been made a subject of conscientious scientific study by certain of the commercial firms which make these cells, and since the cells are now available in rugged form, it is hardly worth the while of an investigator, who is not interested in the cell itself, to undertake the preparation. However a brief description of the preparation may be instructive.

The mercury in the left arm should be carefully purified (page 364) and the same material should be used for the preparation of the cadmium amalgam. This amalgam consists of 12.5[3] per cent by weight of electrolytic cadmium. The amalgam is formed by heating mercury over a steam bath and stirring in the cadmium. Any oxid formed may be strained off by pouring the molten amalgam through a test tube drawn out to a long capillary. An electrolytic method of preparing the amalgam is described by Hulett (1911). Such a method is now used by the Bureau of Standards.

Cadmium sulfate may be recrystallized as described by Wolff and Waters (1907). Dissolve in excess of water at 70°C., filter, add excess of basic cadmium sulfate and a few cubic centimeters of hydrogen peroxid to oxidize ferrous iron, and heat several hours. Then filter, acidify slightly and evaporate to a small volume. Filter while hot and wash the crystals with cold water. Recrystallize slowly from an initially unsaturated solution. The cadmium sulfate solution of a "normal" Weston cell is a solution saturated at whatever temperature the cell is used, and therefore the cell should contain crystals of the sulfate. The ordinary unsaturated cell has a cadmium sulfate solution that is saturated at 4°C.

In the study of Weston cells considerable attention has been paid to the quality of the mercurous sulfate. Perhaps the best and at the same time the most conveniently prepared material is

[3] A 10 per cent amalgam is commonly used in England because it is better adapted to low temperature conditions.

that made electrolytically. Where the alternating current is available it is preferable to use it. A good average set of conditions is a sixty cycle alternating current sent through a 25 per cent sulfuric acid solution with a current density at the electrodes of 5 to 10 amperes per square decimeter. With either the alternating or direct current the apparatus described by fig. 52 is convenient.

In the Weston cell the lead-in wires of platinum should be amalgamated electrolytically by making a wire the cathode in a solution of pure mercurous nitrate in dilute nitric acid.

After filling the cell it may be sealed off in the blast flame or corked and sealed with wax.

In some portable Weston cells of commerce the mercury is introduced as amalgamated electrodes. For a description of commercial cells see Vosburgh and Eppley (1924).

The unsaturated cell is often described as having no temperature coefficient. This is not strictly true. Vosburgh and Eppley (1923) find that the temperature coefficient varies with the electromotive force, being a linear function thereof. For cells with an E.M.F. of 1.01827 it was 0.000,0028 volt per degree. This temperature coefficient declined to $-0.000,013$ per degree for cells with an E.M.F. of 1.0210. Of more practical importance than the temperature coefficient for the whole cell is the fact that it is comparatively small because of the approximate balancing of much larger temperature coefficients for the two half-cells. Hence unequal heating of the two limbs may have a serious effect. In addition there may be some hysteresis during temperature changes. See, for instance, Vosburgh and Eppley (1924). The hysteresis effect is more likely to produce abnormal electromotive forces when the temperature is suddenly lowered than when the temperature is suddenly raised. Because of the abnormalities produced by *temperature changes* it is advisable to protect unsaturated cells against these changes of temperature by some sort of thermal insulation.

As the result of cooperative measurements by the national standards laboratories of England, France, Germany and the United States, and upon agreement as to convention, the normal Weston cell was defined as having the value **1.01830 international volts at 20°C.** Since the value of the international volt

(see page 247) is practically maintained by use of groups of Weston cells maintained at each national standards laboratory, the above definition amounts to a secondary definition of the international volt.

It is important to note that the international agreement came into force January 1, 1911 and that prior to that time the values in force in different countries varied to an extent that makes necessary various corrections in the comparison of the older potential measurements.

TABLE 53a

Increments in the electromotive force of saturated Weston cells when the temperature has been changed and made constant at temperatures other than the standard of reference, i.e., 20°C.

TEMPERATURE	INCREMENT
°C.	volts
5	+0.000,362
10	+0.000,301
15	+0.000,179
20	0.000,000
25	−0.000,226
30	−0.000,491
35	−0.000,789
40	−0.001,112

The temperature coefficient of the normal Weston cell was given by Wolff (1908). The formula which has received international adoption is based on Wolff's formula but has been changed slightly to:[4]

$$E_t = E_{20} - 0.000,040,6 \, (t - 20) - 0.000,000,95 \, (t - 20)^2 + 0.000,000,01(t - 20)^3$$

By this formula the differences in volts from the value at 20°C. are those found in table 53a.

Again it may be emphasized that this formula applies to the *saturated* Weston cell and that ordinarily the comparatively slight temperature coefficient of the unsaturated cell is neglected.

For example, a Weston cell (saturated type) is certified as

[4] Personal communication from Dr. G. W. Vinal, U. S. Bureau of Standards.

having a value of 1.01832 volt at 25°C. Assuming that this particular cell behaves normally its value at 20° should be 1.01855.

While the commercial cells used in the United States are usually of the unsaturated type, those employed in England are said to be usually of the saturated type. Since the question of temperature control has to be given serious consideration in the use of the saturated type and may ordinarily be neglected (except protection from sudden changes) in the use of the unsaturated cell, the purchaser should always be informed of the type.

In certifying cells of the unsaturated type the Bureau of Standards advises the following precautions.

"*Precautions in using standard cells;* (1) The cell should not be exposed to temperatures below 4°C. nor above 40°C., (2) abrupt changes in temperature should be avoided, (3) all parts of the cell should be at the same temperature, (4) current in excess of 0.0001 ampere should never pass through the cell, (5) the electromotive force of the cell should be redetermined at intervals of a year or two."

STORAGE BATTERIES

The storage battery or accumulator is a convenient and reliable source of current for the potentiometer. Standard potentiometers are generally designed for use with a single cell which gives an E.M.F. of about two volts.

The more familiar cell consists of two groups of lead plates immersed in a sulfuric acid solution of definite specific gravity. The plates of one group are connected to one pole of the cell and the plates of the other group are connected to the other pole. When a current is passed through the cell it will produce lead peroxide upon the plates by which the positive current enters and spongy lead upon the other plates. Therefore, on charging, the plates in connection with the positive pole assume the brown color of the oxide while the plates in connection with the negative pole assume the slate color of the spongy metal. The poles should be distinctly marked so that one need not inspect the plates to distinguish the polarity; but, should the marks become obscured and the cell be a closed cell, the polarity should be carefully tested with a voltmeter before attaching the charging current. In lieu of a voltmeter the polarity may be tested with a paper

moistened with KI solution. On applying the terminals to the paper a brown stain is produced at the positive pole. "Positive reaction at positive pole."

In charging a cell the positive pole of the charging circuit should be connected to the positive terminal of the cell, else the cell will be ruined. If a direct current lighting circuit is available, it may be used to charge a cell, or battery of cells, provided sufficient resistance be placed in series.

Resistances are conveniently formed from filament lamps arranged in parallel so that when the bank of lamps is placed in series with the battery and the charging source the introduction of more or fewer lamps will allow more or less current to flow. Much energy is wasted in the resistance which it is necessary to employ when a cell or small battery of cells is charged with a high potential line, and therefore it is more economical to employ low voltage circuits. However these are seldom available.

When only an alternating current is available it is necessary to use some means of changing this to a direct current. The motor-generator may be used; but, with the development of amateur radio and the widespread demand for simple means of charging "A" batteries, several inexpensive rectifiers have become available. These are chiefly of two types. In the one rectification is accomplished with the aid of the electron-valve principle (see page 329). In the other, use is made of the property of the interface between certain metals and an electrolyte solution whereby current will pass chiefly in one direction. These rectifiers are designed for two purposes. Those of larger capacity are designed for the charging of batteries from the condition of discharge to full capacity. Others, of smaller capacity, are designed for that slight recharging at frequent intervals which is sufficient to maintain the battery near complete capacity. The latter type are often referred to as "trickle" chargers.

The electrolyte of the lead cell is pure sulfuric acid solution, the density of which varies with the type and purpose of the cell. The specific gravity of the fully charged cell may vary from 1.210 for stationary batteries to 1.300 for aviation batteries. On discharge the sulfuric acid combines with the active material of the plates and is deposited with a resulting lowering of the specific gravity of the electrolyte. Thus the specific gravity of the elec-

trolyte is highest when the battery is fully charged and lowers during discharge. If there be reason to suspect that the density proper for the type of battery in use is not being maintained, it should be tested with a hydrometer and, in case fresh acid is to be added, only the purest and properly diluted acid should be added. The occasion for this is so rare that ordinarily only pure, distilled water should be added to restore loss by evaporation and gassing. Impurities of the acid or water may have very serious effects upon the conduct and capacity of a cell. None of the substances suggested to improve the electrolyte is necessary and few, if any, have merit.

Among sources of trouble are the following. Overcharging may loosen the active material of the plates. Habitual undercharging may cause excessive accumulation of lead sulfate which, having a larger volume than the original material of the plates, causes mechanical strain and buckling. Corroded terminals may be cleaned with a cloth moistened with ammonia water. The terminals should be covered with vaseline. Defective plates or separators, while sometimes defects of manufacture, may be caused by a variety of mistreatments and usually can be repaired only by opening the cell. If they cause internal short circuits this will be evident by low open circuit voltage. If they cause the elimination of one or more plates from use, the capacity of the cell will be lowered. Excess sulphation may result from neglect. A remedy is to remove the electrolyte, fill the cell with water, place the battery on charge for a long time and finally adjust the specific gravity of the electrolyte to the proper value.

In discharging a cell its voltage should not be allowed to fall below 1.8 volts. When or before the cell has reached this value it should be recharged.

In using a storage cell to supply potentiometer current it is essential that the highest stability in the current should be attained since the fundamental principle of the potentiometer involves the maintenance of constant current between the moment at which the Weston cell is balanced and the moment at which the measured E.M.F. is balanced. Steadiness of current is attained first by having a storage cell of sufficient capacity, and second by using it at the most favorable voltage. Capacity is attained by the number and size of the plates. A cell of 60 ampere-hour capacity is

sufficient for ordinary work. The current from a storage cell is steadiest when the voltage has fallen to 2 volts. When a potentiometer system of sufficient resistance is used it is good practice to leave the cell in circuit, replacing it or recharging it of course when the voltage has fallen to 1.8 or 1.9 volts, and thus insure the attainment of a steady current when measurements are to be made.

In no case should a cell used for supplying potentiometer current be wired so that a throw of a switch will replace the discharging with the charging circuit. The danger of leakage from the high potential circuit is too great a risk for the slight convenience.

Eppley and Gray (1922) replaced the storage battery by a large Weston cell in a special potentiometer circuit but they state that even two of these large cells would not operate a Leeds and Northrup type K potentiometer satisfactorily.

Some of the newer potentiometers are designed to operate with dry-cells.

The alkaline storage cell, sometimes called the nickel-iron cell and known in America as the Edison cell has been used for potentiometer circuits, for example by Gerke and Geddes (1927).

The electrolyte of the Edison cell is usually a solution of potassium hydroxide (plus a small amount of LiOH). The specific gravity does not vary during charge and discharge as it does in the lead cell. Three densities of electrolyte are employed. The "first fill" electrolyte has a specific gravity of 1.228. Spillage is replaced with electrolyte of specific gravity 1.210. After long use and when the specific gravity has fallen to 1.160, there is used a "renewal electrolyte" of specific gravity 1.248.

See also:

Storage Batteries, Vinal (1925). A summary of characteristics operation, etc., prepared for the use of laboratory technicians. Contains a brief bibliography.

CHAPTER XVII

Hydrogen Generators, Wiring, Insulation, Shielding, Temperature Control, Purification of Mercury

Don't descend into the well with a rotten rope.—Turkish Proverb.

hydrogen generators

When there is no particular reason for attaining equilibrium rapidly at the electrode a moderate supply of hydrogen will do. When, however, speed is essential, or when there are used those immersion electrodes which are not well guarded against access of atmospheric oxygen an abundant supply of hydrogen is essential. Indeed it may be said that one of the most frequent faults of the cruder equipments is the failure to provide an adequate supply of pure hydrogen or the failure to use generously the available supply.

Hydrogen generated from zinc and sulfuric acid has been used in a number of investigations. If this method be employed, particular care should be taken to eliminate from the generator those dead spaces which are frequently made the more obvious evidence of bad design, to have an abundant capacity with which to sweep out the gas spaces of cumbersome absorption vessels and to properly purify the hydrogen. To purify hydrogen made from zinc and sulphuric acid pass it in succession through KOH solution, $HgCl_2$ solution, P_2O_5, and platinized asbestos at about 500°C. (See Franzen, Ber., 39, 906) (Heinrich, Ber., 48, 1915, p. 2006).

A very convenient supply of hydrogen is the commercial, compressed gas in tanks. According to Moser (1920) the industrial preparation varies but the chief methods are the electrolytic and the Linde-Caro-Franck processes. Of these the first yields the better product. Hydrogen by the second process contains, among other impurities, iron carbonyl which may be detected by the yellow flame and the deposit of iron oxid formed when the hydrogen flame impinges upon cold porcelain. Moser found that it

was impractical to remove this iron carbonyl and he states that hydrogen containing it is unfit for laboratory purposes. On the other hand, electrolytic hydrogen ordinarily contains only traces
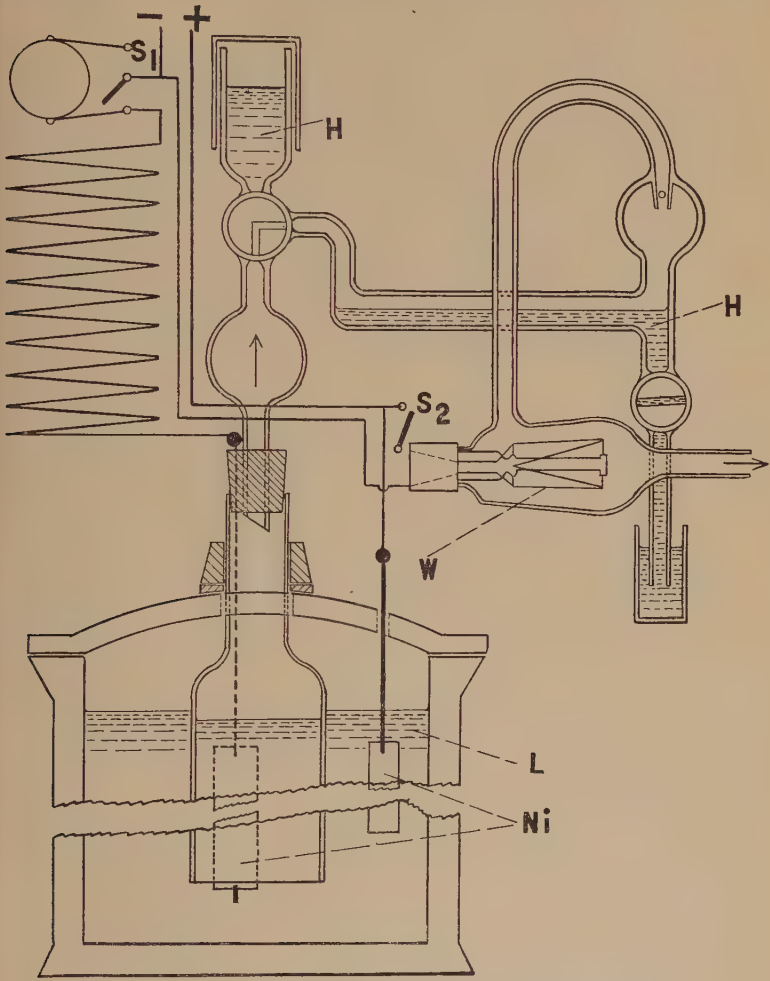
FIG. 66. AN ELECTROLYTIC HYDROGEN GENERATOR

of air and CO_2 and is free from arsenic and CO. To purify it pass the gas over KOH and then through a tube of hot, platinized asbestos. If it is desired to dry the hydrogen, use soda lime or

P_2O_5, but not H_2SO_4.   If P_2O_5 is used it should be free from P_2O_3, i.e., distilled in a current of hot dry air.

In purchasing tank hydrogen it is well to be on guard against tanks which have been used for other gases.

For controlling the flow of gas from a high pressure tank the valve on the tank itself is seldom sufficiently delicate.   There should be coupled to it a delicate needle valve.   If this cannot be obtained use a diaphragm valve for the reduction of the pressure.   Even then there should be placed between the tank and the electrode vessel a T tube, one branch of which dips under mercury and forms a safety valve.

On the whole electrolytic generators are satisfactory if a *direct* current is available.   In figure 66 is shown a generator the body of which is an ordinary museum jar.   The glass cover may be perforated by drilling with a brass tube fed with a mixture of carborundum and glycerine.   If this mixture is kept in place by a ring paraffined in position, and the brass tube is turned on a drill press with intermittent contact of the drill with the glass, the perforation may be made within a few minutes.   The electrolyte used is 10 per cent sodium hydroxid.   The electrodes are nickel.   To remove the spatter of electrolyte and to protect the material in the heater, the hydrogen passes over a layer of concentrated KOH solution, H; and to remove traces of residual oxygen the hydrogen is passed through a heater.   In the design shown the gas passes through a tungsten filament lamp.   Lewis, Brighton and Sebastian use a heated platinum wire.   More commonly there is used a gas-heated or electrically heated tube containing platinized asbestos.[1]

In the author's design shown in figure 66 the wiring is so arranged that, when there is no demand for hydrogen, the heater may be turned off at S_2 and a lamp thrown into series with the generating circuit by switch S_1.   The generator then continues to operate on a low current and sufficient hydrogen is liberated to keep the system free from air.   Such a generator can be run continuously for months at a time.   When in use the generator carries about 4.5 amperes.   If this current be taken from a high voltage lighting system there must be placed in series a proper

[1] Biilmann's interesting remarks on this are cited on page 354.

resistance which can be either built up by a bank of lamps or constructed from nichrome wire.

While it is usually considered good practice to eliminate the residual oxygen from electrolytic hydrogen by the use of some such device as a tube of heated platinized asbestos (see below), there may be occasions when a supply of pure hydrogen direct from the generator is desired. Oxygen may accumulate on the hydrogen side of the generator by diffusion from the oxygen side. This has long been recognized. Biilmann and Jensen (1927) report 0.13 per cent O_2. Gaede (1913) introduced a simple means of prevention. His principle is illustrated in figure 67. A supplementary electrode at C is supplied a small current through resistance R. From this electrode ascend fine bubbles of hydro-
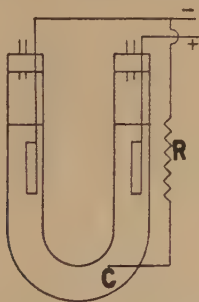
FIG. 67. ILLUSTRATING THE PRINCIPLE OF THE GAEDE-NIESE HYDROGEN GENERATOR

gen which, starting with zero partial pressure of oxygen, "clean up" the residual oxygen diffusing from the oxygen layer above. Niese (1923) describes a more practical generator embodying Gaede's principle. He describes the hydrogen thus obtained as having exceptional purity. Consult citation to Elveden.

Usually investigators have passed the hydrogen through tubes containing platinum in some form which, when heated to about 400°C. very effectively removes residual oxygen. On comparing hydrogen that had passed through platinized asbestos with hydrogen that had passed through platinum gauze Biilmann and Jensen (1927) found that the potential of the cell

$$- \text{Pt}, \text{H}_2 \,|\, \text{HCl} \,(0.1\text{N}), \text{quinhydrone} \,|\, \text{Pt} +$$
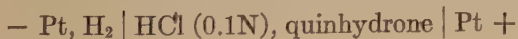
was about half a millivolt higher in the first case than in the second. This they ascribed to a component in the hydrogen from the platinized asbestos that was more active than the hydrogen. They believe it to be silicon hydride. See also their references, and compare with Bach (1925).

Güntelberg (1926) removes residual oxygen from electrolytic hydrogen (he prefers KOH solution) by passing it over copper at 450°C. The copper is pretreated with several oxidations and reductions.

For the conduction of hydrogen over long distances, soft-drawn, seamless, copper tubing is best. That with about 3.2 mm. external diameter is satisfactory. Where this is to be joined to a metal connection, silver solder[2] applied with borax flux is preferable to tin-lead solder, since the latter type of junction is apt to

BRASS SLEEVE   GLASS TUBE
COPPER TUBE   SILVER SOLDER
DE KHOTINSKY CEMENT

Fig. 68. Junction of Copper and Glass Tubes

contain "pin-holes." Where the copper tube is to be joined to glass tubing use a piece of brass like that of figure 68. This is quickly turned on the lathe. The copper tube is first silver-soldered to the brass sleeve. The copper tube should not fit too loosely. If the metal is very hot when the solder flows, silver solder will run *into* the junction nicely. To join with the glass tube, warm both brass tube and glass tube, smear each with hot deKhotinsky cement and slip the two together. The interior diameter of the sleeve should be little larger than the glass tube. Extra cement is then moulded, while warm, about the whole joint in order to strengthen it mechanically.

[2] Silver solder: composed of 6.5 parts copper, 2.0 parts zinc and 11.0 parts silver. This solder is described as fusing at about 983°C. A nickel wire is useful in spreading the flux and solder. The flux is prefused borax. The heat of a blast lamp is required. Hardware stores carry the solder.

For the more elaborate trains there may be used standard "$\frac{1}{8}$ inch," bronze cocks of the type with ground keys under spring tension. These are furnished with all sorts of ends for use with standard "$\frac{1}{8}$ inch" pipe fittings and with attachments for either the so-called "compression" or the "soldered connection" with copper tubing. See for instance the catalogue of the Lunkenheimer Company, Cincinnati.

WIRING

Whenever a set-up is to be made more than an improvisation it pays to make a good job of the wiring. A poor connection may
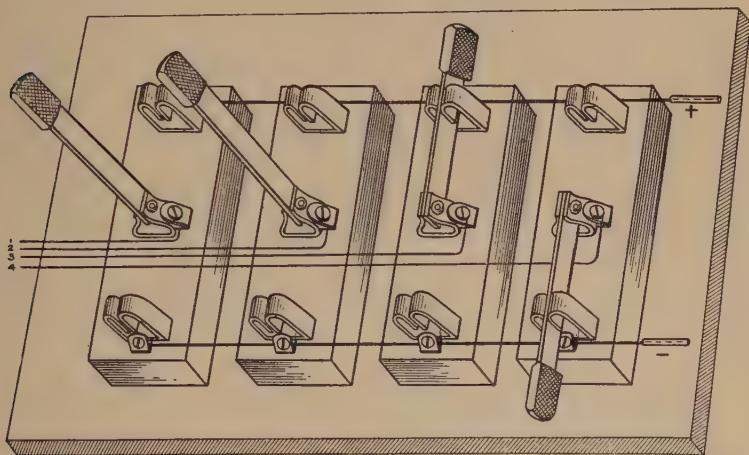
Fig. 69. Switches for Connecting Half-Cells with Potentiometer

be a source of endless trouble and unsystematized wiring may lead to confusion in the comparison of calomel electrodes and the application of corrections of wrong sign.

Soldered connections or stout binding posts that permit strong pressure without cutting of the wire are preferable to any other form of contact. If for any reason mercury contacts are used they had best be through platinum soldered to the copper lead. Copper wires led into mercury should not take the form of a siphon else some months after installation it may be found that the mercury has been siphoned off.

Thermo-electromotive forces are seldom large enough to affect

measurements of the order of accuracy with which we are now concerned if care be taken to make contacts so far as possible between copper and copper at points subject to fluctuations in temperature.

A generous use of copper knife switches can be made to contribute to the ease and certainty of check measurements. For instance if there be a battery of hydrogen electrodes and a set of calomel electrodes, wires may be led from each to a centre connection of single-pole, double-throw switches as shown in figure 69. All the upper connections of these switches are connected to the + pole of the potentiometer's E. M. F. circuit, and all the lower connections to the − pole. By observing the rule that no two switches shall be closed in the same direction, short-circuiting of combinations is avoided. The position of a switch shows at once the sign of the metal of the attached half-cell in relation to any other that may be put into liquid junction. This is a great convenience in comparing calomel electrodes where one half-cell may be positive to another and negative to a third. Such a bank of single pole switches permits the comparison of any electrode with any other when liquid junction is established; and, if a leak occur in the electrical system, the ability to connect one wire at a time with the potentiometer and galvanometer often helps in the tracing of the leak.

INSULATION

For wires perhaps the most satisfactory insulation for general use is pliable rubber. The textiles are unsatisfactory in damp weather and although paper is used very successfully in telephone cables where close packing is desired it must be protected absolutely from dampness. Even the terminals of the lead covered cables must be boxed. Enameled wire, the enamel of which can be tested for leaks by obvious connections made while the wire is run through a mercury bath, makes very pretty wiring.

In ordinary potentiometric measurements, but especially in the operation of an electrometer, the high intrinsic insulating qualities of materials which are of supreme importance in high tension work, may become of secondary importance compared with surface leakages. Cleanliness of supports is therefore a part of good technique, for accumulation of dirt may enhance the con-

ductivity of surface films of moisture. As far as moisture films are concerned paraffin, if kept clean, is an excellent preventive of excess trouble for moisture does not "film out" very well on its surface.   Of the same properties, but preferred for its mechanical strength, is mineral paraffin known as ozokerite. When such surfaces become dirty they should first be wiped and then flamed wherever this is practicable.

The insulating material frequently used for the machined parts of instruments, e.g., the plate of a potentiometer, is hard rubber. The qualities of such rubber vary widely.   While it usually has a high insulating value this may become impaired and the surface may become unsightly by the oxidation of its sulfur under the action of light. I know of no satisfactory remedy. A preventive is the protection from light.

Bakelite is replacing rubber for many purposes and since the advent of amateur radio it is readily available in sheets which can be cut to good purpose in the installation and wiring of a potentiometer equipment.

For some of the extreme measures necessary in the operation of the glass electrode with an electrometer as null-point instrument, see Kerridge (1926) and Brown (1924).

SHIELDING

Electrical leaks from surrounding high potential circuits are sometimes strangely absent from the most crude systems and sometimes persistently disconcerting if there is not efficient shielding.   The principle of shielding is based on the following considerations.   If between two supposedly well-insulated points on a light or heating circuit, or between one point of such a circuit and a grounding such as a water or drain pipe, there is a slight flow of current, the electrical charges will distribute themselves over the surface films of moisture on wood and glass-ware.   At two points between which there is a difference of potential the wires of the measured or measuring system may pick up the difference of potential to the detriment of the measurement.   If however *all* supports of the measured and measuring systems lie on a good conductor such as a sheet of metal, the electrical leakage from without will distribute itself over an *equipotential* surface and no differences of potential can be picked up.   To shield

efficiently, then, it is necessary that *all* parts of the system be mounted upon metal that can be brought into good conducting contact. In many instances the complications of hydrogen electrode apparatus and especially the separation of potentiometer from temperature bath make a simple shielding impracticable. Care must then be taken that all of the separate parts are well connected. Tinfoil winding of *insulated* wire in contact with unshielded points can be soldered to stout wires for connection to other parts by dropping hot solder on the well-cleaned juncture.

Flexible, rubber-covered wire with a spirally wound armor is especially valuable for shielded connections. It is sold for automobile connections.

Shielding should not be considered as in any way taking the place of good insulation of the constituent parts of the measured or measuring systems.

For further details in regard to shielding see W. P. White (1914).

TEMPERATURE CONTROL

Baths

Temperature control is a matter where individual preference holds sway. There are almost as many modifications of various types of regulators as there are workers. Even in the case of electrical measurements where orthodoxy interdicts the use of a water bath it has been said (Fales and Vosburgh and others) that it can be made to give satisfaction.

Yet there are a few who may actually make use of a few words of suggestion regarding temperature control for hydrogen electrode work.

As a rule the water bath is not used because of the difficulty of preventing electrical leakage. Some special grades of kerosene are sold to replace the water of an ordinary liquid bath but for most purposes ordinary kerosene does very well. The free acid sometimes found in ordinary kerosene may injure fine metallic instruments. To avoid this, use the grade sold as "acid-free, medium, government oil."

A liquid bath has the advantage that the relatively high specific heat of the liquid facilitates heat exchange and within a half hour or so brings material to the controlled temperature, but

compared with an air bath it has the disadvantage that stopcocks
must be brought up out of the liquid to prevent the seepage of the
oil.   The advantage of the high specific heat of a liquid is falsely
applied when the constancy of a liquid bath is considered to be a
great advantage over the more inconstant air bath.   The lower
the specific heat of the fluid the less effect will variation in the
temperature of that fluid have upon material which has already
been brought to and is to be kept at constant temperature.   For
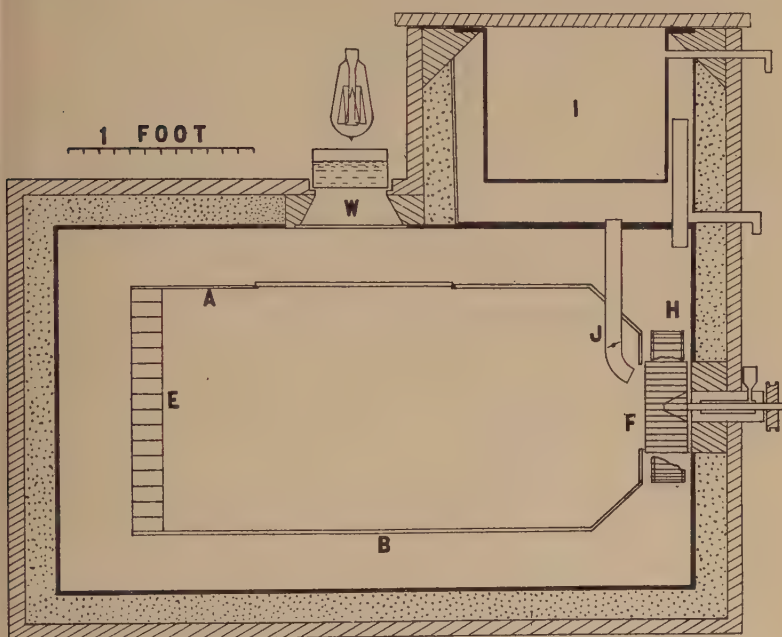
FIG. 70. CROSS-SECTION OF AN AIR BATH

this reason a well-stirred air bath whose temperature may oscillate
about a well-controlled mean may actually maintain a steadier
temperature in the material under observation than does a liquid
bath which itself is more constant.   It is the temperature of the
material under observation and not the temperature of the bath
which is of prime interest when the temperature is once attained.

An air bath can be made to give very good temperature control
and since it is more cleanly than an oil bath and permits direct-

ness and simplicity in the design of apparatus a brief description of one form used by the writer for some years may be of interest.

A schematic longitudinal section illustrating the main features is shown in figure 70.

The walls of the box are lined with cork board finished off on the interior with "transite." The front is a hinged door constructed like the rest of the box but provided with a double glass window and three 4-inch hand holes through which apparatus can be reached. On the interior are mounted the two shelves A and B extending from the front to the back wall and providing two flues for the air currents generated by the fan F.

The writer at one time used a no. 0 Sirocco fan manufactured by the American Blower Company, demounted from its casing and mounted in the bearing illustrated. He now uses a four-blade fan taken from a desk-fan and mounted so that it turns in the hole F of the partition and blows toward E. The baffle plates at E, made of strips of tin arranged as in an egg-box, and intended to establish parallel lines of flow when the centrifugal fan was used, are now eliminated.

In the illustration the oil cup is shown as if it delivers into an annular space cut out of the Babbit-metal bearing. In reality this annular space is provided by cutting away a portion of the steel shaft.

The heating of the air is done electrically with the use of bare, nichrome wire of no. 30 B. and S. gauge. When using the centrifugal fan the wire is strung between rings of asbestos board (the hard variety known as "transite" or "asbestos wood") which fit over the fan at H. With the blade-fan the partition at F is made of asbestos board and the wire is strung over the opening. The air is thus heated at its position of highest velocity. The electrical current in this heating coil can be adjusted with the weather so that the time during which the regulator leaves the heat on is about as long as the time during which the regulator leaves the heat off. In other words adjustment is made so that the heating and cooling curves have about the same slope.

When the room temperature is not low enough to provide the necessary cooling the box I is filled with ice water. Surrounding this is an air chamber into which air is forced from the high pressure side of the fan. J should be provided with a damper which

can easily be reached and adjusted. A loop of copper tubing carrying cold water near the heating wires would probably do as well.

To lessen danger of electrical leakage over damp surfaces the air is kept dry by a pan of calcium chlorid placed under B.

A double window at W over which is hung an electric light provides illumination of the interior. A solution of a nickel salt is placed at this window to absorb the heat from the lamp.

The double window in the door (not shown) should be beveled toward the interior to widen the range of vision.

Such a box has been held for a period of eight hours with no change which could be detected by means of a tapped Beckmann thermometer and with momentary fluctuations of $0.003°$ as determined with a thermo-element. The average operation is a temperature control within $\pm 0.03°$ with occasional unexplained variations which may reach $0.1°$. *Because of the slowness with which air brings material to its temperature, the air bath is continuously kept in operation, and if a measurement is to be made quickly the solution is preheated to the desired temperature.*

Regulators

Given efficient stirring and a considerate regulation of the current used in heating, accurate temperature control reduces to the careful construction of the regulator. The ideal regulator should respond instantaneously. This implies rapid heat conduction. Regulators which provide this by having a metal container have been described but glass will ordinarily be used. At all events there are two simple principles of regulator construction the neglect of which may cause trouble or decrease sensitivity and attention to which improves greatly almost any type. The first is the protection of the mercury contact from the corroding effect of oxygen. The second is the elimination of platinum contacts which mercury will soon or later "wet," and the substitution of an iron, nickel or nichrome wire contact.

After trials of various designs the author has adopted the form of regulator head shown in figure 71. (See Clark, 1913.)

Pyrex glass is used in its construction. To seal the platinum lead at P a very fine wire is used and the seal is made mechanically strong by a sufficient thickness of glass. Although such a seal

will usually not be vacuum-tight it can be made so by having the mercury in the exterior arm during the evacuation presently to be mentioned. Preparatory to filling the bulb the glass side arm is constricted at D as a preliminary to sealing; beyond this constriction it is drawn off to a fine capillary E. The head is then attached to a pump and the apparatus exhausted. Then the capillary side arm is broken under a reservoir of carefully purified mercury. If the exhaustion has been well done, mercury will fill the vessel with practically no gas bubbles left. The vessel is then detached from the pump and a stream of pure hydrogen is swept through the head entering at E. There has previously been prepared the contact wire of "Chromel" alloy. This should be large enough to fill the capillary at A nearly completely. However, its tip, to make contact at B, is etched with aqua regia until it gives ample space for the mercury column. If it takes too much space in the capillary at B, mercury will be squeezed off as drops when it rises with overheating. With the wire in place, deKhotinsky cement is melted at K, with care to prevent it creeping to the bulb below. Meanwhile the hydrogen pressure is kept from building up by escaping through a trap. The side arm is now sealed at D. Ample excess mercury has been left and this is now thrown into the side arm as shown. Rough adjustment is made by throwing mercury in or out of this reservoir. Fine adjustments are made by warming the cement at K and raising or lowering the wire. When adjusted the wire is clamped in the chuck C, designed by A. H. Thomas Company, or simply held by the cement. The capillary at B and the size of the mercury bulb can be adjusted to requirements.

For discussion of other regulators and principles of thermostat control see numerous references in Chemical Abstracts and, for example, Tian (1923).

FIG. 71. A TEMPERATURE REGULATOR

(After Clark (1913). Drawing by Courtesy A. H. Thomas Company)

HEAT CONTROL

For electrical heating, the control system shown in figure 72 is simple and effective. The current from the main, M, passes through a bank of lamps L to the heater by way of H. Lamps are used since they provide a convenient variety of resistance adjustable to the current desired. The current is thrown on or off by the relay, R, controlled by current from the regulator connected to T. To lower sparking the gap at the relay is shunted by lamp B. If direct current is available it may be used for the operation of the relay by drawing a low potential circuit from the resistance O. In case only alternating current is available a storage battery is placed in series with the relay and thermoregulater T. Too strong a current is to be avoided. A sharp, positive action of
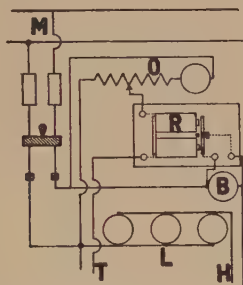
FIG. 72. WIRING FOR HEAT-CONTROL BY RELAY

the relay should be provided against the day when the relay contact may become clogged with dust. To reduce sparking at the regulator and at the relay contacts, inductive coils in the wiring should be avoided. Spanning the spark gaps with properly adjusted condensers made of alternate layers of tin foil and paraffin paper may eliminate most of the sparking, if the proper capacity be used.

For relay contacts the tungsten contacts used in gas engines are very good.

For heaters to be used in water baths electric filament lamps are frequently used. With oil baths, base "Chromel" alloy may be used. This should be kept immersed and the leads made heavy. For good regulation it is essential to adjust the current until the heating rate is about the same as the cooling rate. This

is easily determined by noting the number of lamps used in series with the heater when the current is on about the same length of time it is off.

PURIFICATION OF MERCURY

Pure mercury is essential for many purposes in hydrogen electrode work,—for the calomel and the mercury of calomel electrodes, for Weston cells should these be "home made," for thermoregulators and for the capillary electrometer.

The more commonly practiced methods of purification make use of the wide difference between mercury and its more troublesome impurities in what may be descriptively put as the "electrolytic solution tension." Exposed to any solution which tends to dissolve base metals, the mercury will give up its basic impurities before it goes into solution itself, provided of course the reaction is not too violent for the approach to equilibrium conditions.

The most commonly used solvent for this purpose is slightly diluted nitric acid although a variety of other solutions such as ferric chloride may be used.

To make such operations efficient it is necessary to expose as large a surface as possible to the solution. Therefore the mercury is sometimes sprayed into a long column of solution which is supported by a narrow U-tube of mercury. The mercury as it collects in this U-tube separates from the solution and runs out into a receiver. To insure good separation the collecting tube should be widened where the mercury collects but this widening should not be so large as to prevent circulation of all the mercury. A piece of very fine-meshed silk tied over the widened tip of a funnel makes a fine spray if the silk be kept under the liquid. This simple device can be made free from dead spaces so that all the mercury will pass through successive treatments. It is more difficult to eliminate these dead spaces in elaborate apparatus; but such apparatus, in which use is made of an air lift for circulating the mercury, makes practicable a large number of treatments. A combination of the air lift with other processes and a review of similar methods has been described by Patten and Mains (1917).

Hulett's (1905, 1911) method for the purification of mercury consists in distilling the mercury under diminished pressure in a current of air, the air oxidizing the base metals. Any of these

oxids which are carried over are filtered from the mercury by pass-
ing it through a series of perforated filter papers or long fine cap-
illaries.   A convenient still for the purpose is made as follows.
Fuse to the neck of a Pyrex Kjeldahl flask a tube about 30 cm.
long which raises out of the heat of the furnace the stopper that
carries the capillary air-feed.   Into the neck of the flask fuse by
a T-joint seal a 1.5 cm. tube and bend this slightly upward for a
length of 15 cm. so that spattered mercury may run back.   To the
end of this 15 cm. length join the condensing tube, which is simply
an air condenser made of a meter length of tubing bent zigzag.
Pass the end of this through the stopper of a suction flask and
attach suction to the side tube of this flask.   The mercury in the
Kjeldahl flask may be heated by a gas flame or an electric furnace.
For a 220 volt D. C. circuit 12 meters of no. 26 nichrome (Chromel)
wire wound around a thin asbestos covering of a tin can makes
a good improvised heating unit if well insulated with asbestos or
alundum cement.   A little of this cement applied between the
turns of wire after winding will keep the wire in place after the
expansion by the heat.

In the construction of such stills it is best to avoid soft glass
because of the danger of collapse on accidental over-heating.
Hostetter and Sosman describe a quartz still.

Both the air current, that is delivered under the surface of the
mercury by means of a capillary tube, and the heating should be
regulated so that distillation takes place smoothly.

Since it is very difficult to remove the last traces of oxid from
mercury prepared by Hulett's distillation the author always makes
a final distillation in vacuo at low temperature.   An old but good
form of vacuum still is easily constructed by dropping from the
ends of an inclined tube two capillary tubes somewhat over baro-
metric length.   One of these is turned up to join a mercury res-
ervoir, the other, the condenser and delivery tube, is turned up
about 10 cm. to prevent loss of the mercury column with changes
in external pressure.   The apparatus is filled with mercury by suc-
tion while it is inclined to the vertical.   Releasing the suction
and bringing the still to the vertical leaves the mercury in the
still chamber supported by a column of mercury resting on atmos-
pheric pressure and protected by the column in the capillary
condenser.   The heating unit is wire wound over asbestos.   The

heat should be regulated by a rheostat till the mercury distills very slowly. By having the mercury condense in a capillary the still becomes self-pumping.

CAUTION

Perhaps few of us who work with mercury have a proper regard for the real sources of danger to health. The vapor pressure of mercury at laboratory temperatures is not to be feared, but emulsification with the dust of the floor may subdivide the mercury until it can float in the air as a distinct menace. Its handling with fingers greasy with stop cock lubricant is also to be avoided on account of possible penetration of the skin but more particularly because of the demonstrated ease with which material on the hands reaches the mouth.

CHAPTER XVIII

OXIDATION-REDUCTION POTENTIALS

We must remember that we cannot get more out of the mathematical mill than we put into it, though we may get it in a form infinitely more useful for our purpose.—JOHN HOPKINSON.

THE RELATION OF HYDROGEN ELECTRODE POTENTIALS TO REDUCTION POTENTIALS

The hydrogen electrode is constructed of a noble metal laden with hydrogen, and it may be asked what relation it bears to those electrodes which consist of the noble metal alone and which are used to determine the so-called oxidation-reduction potentials of solutions of mixtures such as ferrous and ferric iron.

If a platinum or gold electrode be placed in an acid solution of ferrous and ferric chlorides there will almost immediately be assumed a stable potential which is determined by the *ratio* of the ferrous to the ferric *ions*. The relation which is found to hold is given by the equation:

$$E_h = E_o - \frac{RT}{nF} \, ln \, \frac{[Fe^{++}]}{[Fe^{+++}]} \tag{1}$$

where E_h is the observed potential difference between the electrode and the standard normal hydrogen electrode, E_o is a constant characteristic of this particular oxidation-reduction equilibrium and equal to E_h when the ratio $\frac{[Fe^{++}]}{[Fe^{+++}]}$ is unity, R, T, n and F have their customary significances, and $[Fe^{++}]$ and $[Fe^{+++}]$ represent concentrations of the ferrous and the ferric ions respectively. This equation will be referred to later as Peters' (1898) equation. Its general form is:

$$E_h = E_o' - \frac{RT}{nF} \, ln \, \frac{[Red]}{[Ox]} \tag{2}$$

where [Red] represents the concentration of the reductant and [Ox] represents the concentration of the oxidant.
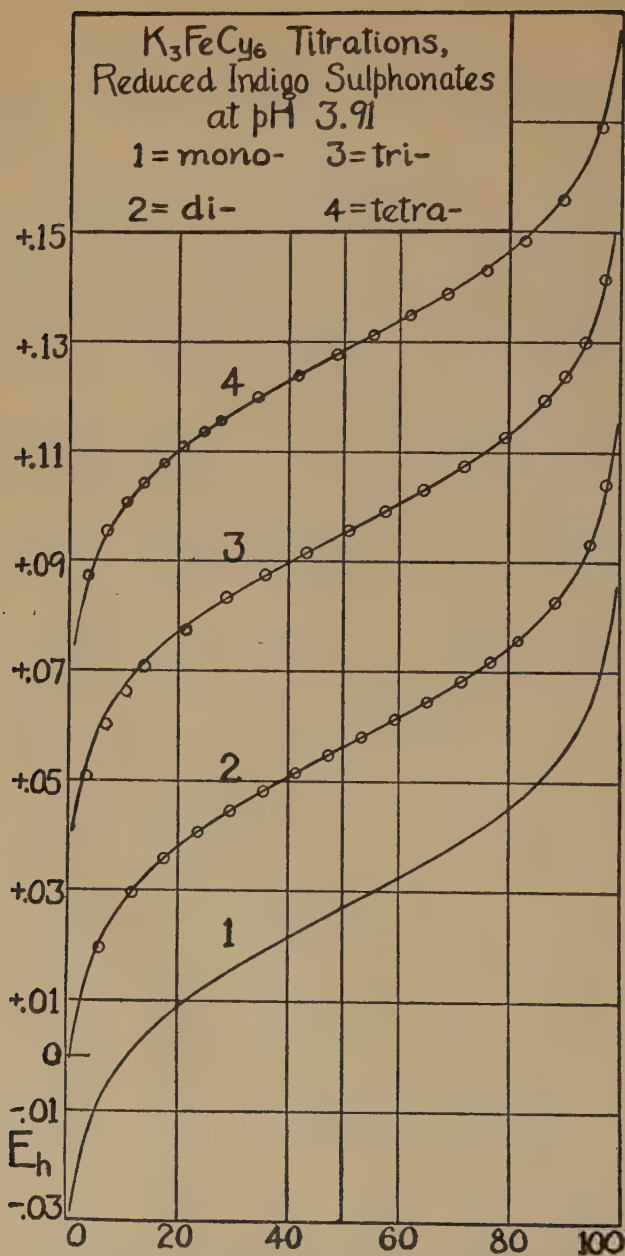
FIG. 73. RELATION OF ELECTRODE POTENTIAL, E_h, TO PERCENTAGE
OXIDATION AT CONSTANT pH

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If we plot E_h on one coordinate and the percentage reduction on the other coordinate, we obtain a set of curves identical in form for a given value of n. The position of each curve along the E_h axis is determined by the value of E_o' which fixes the middle point and thereby places the curve of a specific system.

Such curves for four different systems are shown in figure 73. In these cases the hydrion concentration was held constant for reasons which will appear later. Each of these particular curves has the slope characteristic of an oxidation-reduction system in which the transformation of oxidant to reductant involves at one and the same step two electrochemical equivalents. That is, n, in equation (2), has the value 2. With the noteworthy exception that these titration curves reveal no stepwise oxidation, they are *analogous to* the curves for acid-base equilibria described in Chapter I.

It will be clearly understood that in using the term "oxidation" or the term "oxidant" we do not imply that oxygen is necessarily concerned. Oxidation is one of those terms established under an old order of thought and carried into a new order with its meaning broadened. As CO_2 is a "higher" oxide of carbon than CO it is natural to regard the process represented by $2CO + O_2 \rightarrow 2CO_2$ as an *oxidation*. The reverse process, which leads to reduction in the degree of oxidation, is naturally called *reduction*. At one time it was seen fit to classify certain types of chemical change in terms of the participation of oxygen. A schematicized representation of the transformation of ferrous to ferric iron may be based upon this practice.

$$\leftarrow \text{reduction}$$
$$\text{oxidation} \rightarrow$$
$$2FeO \;+\; O \;\rightleftharpoons\; Fe_2O_3$$

| solution | $+$ | | $+$ | solution |

$$4HCl \qquad\qquad 6HCl$$
$$\downarrow \qquad\qquad\quad \downarrow$$
$$2FeCl_2 \qquad\qquad 2FeCl_3$$

| ionization | $\downarrow$ | | $\downarrow$ | ionization |

$$2Fe^{++} \;\rightleftharpoons\; 2\epsilon \;+\; 2Fe^{+++}$$
$$\text{OXIDANT}$$
$$\leftarrow \text{reduction}$$
$$\text{oxidation} \rightarrow$$
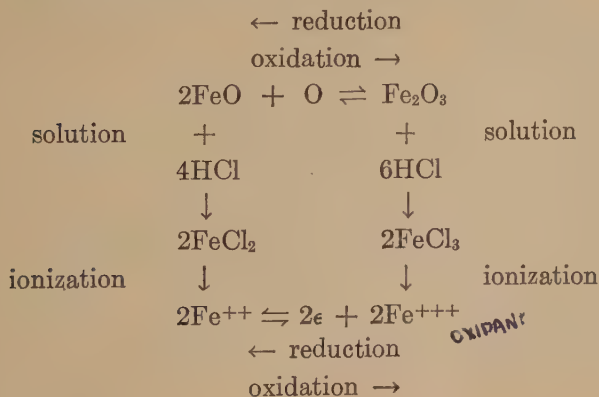
Neglecting the by-products in the above reactions and concentrating attention upon the states of the iron, we see that Fe^{+++} may be related to the higher oxide and Fe^{++} may be related to the lower oxide. Hence Fe^{+++} may be called the oxidant and Fe^{++} the reductant of the system Fe^{+++}: Fe^{++}. Through a variety of such schemes a number of transformations which are now conveniently pictured as mere gain or loss of electrons are described as reductions and oxidations respectively. For somewhat more detail see Clark (1923).

The term "reduction" does not, in itself, imply any relation to the participation of hydrogen; but it is often assumed that hydrogen is concerned in reduction in much the same way that oxygen was thought to be concerned in every "oxidation."

Before coming to a more generalized presentation we shall describe the relation between the hydrogen electrode and the oxidation-reduction electrode *in terms of* hydrogen and hydrogen ions.

It is known that certain reducing agents are so active that they evolve hydrogen from aqueous solutions. In such a solution an electrode would become charged with hydrogen and would conduct itself much like a hydrogen electrode. The relations then obtaining can be extended and, if we wish to represent the interaction of the reducing agent with the hydrogen ions, we have:

$$H^+ + \text{reducing agent} \rightleftharpoons H + \text{oxidation product}$$
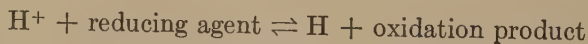
If equilibrium is established for the above reaction

$$\frac{[H^+]\,[Red]}{[H]\,[Ox]} = K$$

$$K\,\frac{[H]}{[H^+]} = \frac{[Red]}{[Ox]}$$

Substituting $K\,\dfrac{[H]}{[H^+]}$ for the ratio $\dfrac{[Red]}{[Ox]}$ in Peters' equation, (2), and placing $n = 1$ for the case at hand we have

$$E_h = E_o' - \frac{RT}{F}\,ln\,K\,\frac{[H]}{[H^+]}$$

Since the atomic hydrogen bears a definite relation to the partial pressure of molecular hydrogen, P, through the equilibrium expressed by;

$$[H]^2 = K_h P,$$

we may substitute, collect constants under another constant K', combine E_o' and $ln\ K'$ as E_o and obtain

$$E_h = E_o - \frac{RT}{F} ln\ \frac{\sqrt{P}}{[H^+]} \tag{3}$$

Compare this with the general relation for the hydrogen electrode

$$E_h = E_H - \frac{RT}{F} ln\ \frac{\sqrt{P}}{[H^+]} \tag{4}$$

E_H in (4) is zero *by definition* when there is used the "normal hydrogen electrode" system of reference. When (3) is placed on the same basis E_o is also zero, since each of the other terms in (3) is identical with the corresponding term in (4).

In other words we have substituted for the oxidation-reduction equilibrium the corresponding point of equilibrium between hydrogen and hydrogen ions, and have considered the potential difference at the electrode as if it were that of a hydrogen electrode. An inference is that wherever we have an oxidation-reduction equilibrium the components will have interacted with hydrogen ions (or water) liberating free hydrogen and building up at the electrode a definite pressure of hydrogen. Conversely, if hydrogen is already present at the electrode with a pressure too high for the oxidation-reduction equilibrium in question, hydrogen will be withdrawn until its pressure is in harmony with the oxidation-reduction equilibrium (the position of the latter having been shifted more or less by reduction). When a constant pressure of hydrogen is maintained at the electrode, as it is in the customary use of the hydrogen electrode, no true equilibrium can be attained until this hydrogen has so far reduced all the substances in the solution that they can support one atmosphere pressure of hydrogen.

Incidentally it may be mentioned that it is a matter of indiffer-

ence whether we regard the reductant to interact with the hydrogen ions or the oxidant with the hydroxyl ions or each with water. By use of the equilibrium equations which are involved we reach the same end-result whatever the path.

Furthermore by the use of certain theoretical relations between the hydrogen electrode and the oxygen electrode we could *define* a potential in terms of that of an oxygen electrode.

This method of relating oxidation-reduction equilibria to electrode potentials is convenient for showing the condition which must obtain for a true hydrogen electrode potential; but when we attempt to follow some of the logical consequences of this, the customary exposition, we not only meet some serious difficulties but obscure some very important relations.

Let us calculate the hydrogen pressure in equilibrium with an equimolecular mixture of ferrous and ferric chlorid in a solution held at pH 1. A platinum electrode in such a solution will have a potential about 0.75 volt more positive than the "normal hydrogen electrode." Let us consider this to be the difference of potential between a hydrogen electrode at pH 1 and a normal hydrogen electrode. Let us calculate, then, the hydrogen pressure at 25°C. from the equation:

$$0.75 = -\ 0.059 \log \frac{\sqrt{P}}{0.1} \tag{5}$$

We find the hydrogen pressure to be about 10^{-27} atmospheres. At one atmosphere pressure a mole of hydrogen occupies about 22 liters and contains about 6×10^{23} molecules. If the pressure is reduced to 6×10^{-23} atmospheres there would be but *one molecule* of hydrogen in 22 liters. If reduced to 10^{-27} atmospheres there would be but *one molecule* in about 37,000 liters. To assume any physical significance in such values is, of course, ridiculous. It is only by courtesy then that an electrode in a mixture of ferrous and ferric iron at pH 1 can be considered as a hydrogen electrode.

FORMULATION BY USE OF ELECTRON TRANSFER

The problem of mechanism suggested above will not be solved by the following *formal* treatment; but this treatment may aid the student to retain an orderly view of important relations, and

it will provide a basis on which to discuss the interrelations of electrodes of different type. When this interrelation is understood a more generalized point of view is easier to attain.

It is generally agreed that *one* of the fundamental parts of an oxidation-reduction process is an exchange of electrons. Although too great an emphasis on this as a reality may be objectionable, the objection is not relevant to our present purpose,— the *organization* of relations.

We shall use the concept as a means of developing several different equations by a common route. On entirely different grounds we shall return to the discussion of actuality later.

An example of a process involving electron exchange is:

$$\text{Ferric ion} + \text{electron} \rightleftharpoons \text{ferrous ion}$$
$$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$$
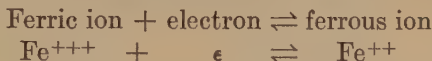
Since such a reversible reaction is not dependent upon the presence of an electrode (acting as a catalyst) it is probable that an exchange of electrons is going on continuously. There must then be some condition virtually equivalent to a free-electron pressure. If we desire a mechanistic picture we may imagine a moment in the exchange during which the electron is balanced between the forces of each ion. At this moment the electron may be considered to belong to neither ion and to be a property of the environment. Undoubtedly the situation is not so simple as this picture suggests; and, although the presence of free electrons has been demonstrated in liquid ammonia and methylamine solutions, the experimental evidence is not sufficient to justify our assuming the presence of free electrons in aqueous solutions to be a fact. However, it may be said at once that we are not now concerned with the objective actuality of a "freedom." A pressure of *free* electrons may be postulated as the virtual equivalent of a condition not yet clearly formulated; it may be used in much the same way that Nernst used "solution tension,"— destined from the first to be eliminated from those equations which are employed to formulate experimental data.

An electron escaping tendency may be postulated without necessarily implying appreciable numbers of *free* electrons and without immediate investigation of the source of the electrons which are transferred from one system to another when the oxi-

dant and reductant of one system interact with the oxidant and reductant of another system.

Imagine an aqueous solution of ferrous- and ferric chlorides in which there is, initially, an exact equivalence between the positive charges carried by all cations and the negative charges carried by all anions. If an electron should leave a ferrous ion without passing over to a ferric ion (thereby creating a new ferrous ion to take the place of the first) no disturbance of the solution's electroneutrality would occur. There would still be equivalence of positive and negative charges. The same would be true if the ferrous and ferric ions reacted with components of the solution as

$$Fe^{++} + H^+ \rightleftharpoons Fe^{+++} + H$$
$$Fe^{++} + Cl \rightleftharpoons Fe^{+++} + Cl^-$$

We are evidently not concerned with ordinary, electrostatic affairs.

There might be expected some degree of action between the iron ions and components of the solution in the sense written above. However, it has already been indicated (page 372) that the action of ferrous ions on hydrions to form hydrogen and ferric ions cannot be appreciable. Indeed we shall anticipate a conclusion to be drawn when the formulation is complete and the data are at hand. We shall state that no appreciable chlorine would be formed from the second of the above reactions. In general none of the oxidation-reduction systems to be considered *in this section* acts appreciably on other components of the solutions to be considered.

Therefore, in an acid[1] solution of ferric and ferrous chlorides, we shall consider the oxidation-reduction system to be exclusively that represented by
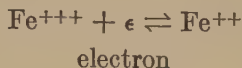
$$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$$
electron

[1]Acid to prevent hydrolysis and the formation of $Fe(OH)_2$ and $Fe(OH)_3$. The participation of these and other complexes is considered in a separate section.

This we shall call the "iron system."   The equilibrium state
we shall describe by

$$\frac{(Fe^{+++})\,(\epsilon)_{Fe}}{(Fe^{++})} = K_{Fe} \qquad (6)$$

Where ( ) represents activity and $(\epsilon)_{Fe}$ is the electron activity[2] in
the iron solution.

Next imagine another oxidation-reduction system described by

$$2H^+ + 2\epsilon \;\rightleftarrows\; H_2$$
$$\text{hydrion}\quad\text{electron}\quad\text{hydrogen}$$
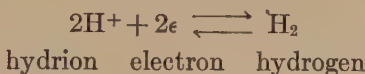
This we shall call the hydrogen system.

Knowing that hydrogen by itself acts *slowly*, we may assume,
in the following discussion, the presence of a catalyst that will
always insure the attainment of the equilibrium states to be con-
sidered.   For convenience we shall use hydrogen pressure, P,
(in atmospheres) in defining the equilibrium equation.

$$\frac{(\epsilon)_H\,(H^+)}{\sqrt{P}} = K_H \qquad (7)$$

For the transfer of **F** (one faraday) electrons from activity
$(\epsilon)_H$ to activity $(\epsilon)_{Fe}$

$$-\,\Delta F = \mathbf{E}\,\mathbf{F} = RT\,ln\,\frac{(\epsilon)_H}{(\epsilon)_{Fe}} \qquad (9)$$

Where **E** is the electromotive force in volts.

Substitute in (9) the equivalents of $(\epsilon)_H$ and $(\epsilon)_{Fe}$ from equa-
tions (6) and (7)

$$\mathbf{E} = \frac{RT}{F}\,ln\,\frac{K_H\,\sqrt{P}\,(Fe^{+++})}{K_{Fe}\,(H^+)\,(Fe^{++})} \qquad (10)$$

Rewrite (10) as (13) where

$$\mathbf{E}_H = \frac{RT}{F}\,ln\,K_H \qquad (11)$$

[2] The electron activity need not be defined.   It is a tentative expedient
destined from the first to be eliminated from the final equations.   But
see page 376.

and

$$E_{Fe} = \frac{RT}{F} \, ln \, \frac{1}{K_{Fe}} \qquad (12)$$

$$E = E_H + E_{Fe} + \frac{RT}{F} \, ln \, \frac{\sqrt{P}}{(H^+)} + \frac{RT}{F} \, ln \, \frac{(Fe^{+++})}{(Fe^{++})} \qquad (13)$$

We shall now make the definition that when $P = 1$ and when $(H^+) = 1$, $(\epsilon)_H = 1$. Then by (7) $K_H = 1$ and by (11) $E_H = 0$. Equation (13) may then be written

$$E_h = E_{Fe} - \frac{RT}{F} \, ln \, \frac{(Fe^{++})}{(Fe^{+++})} \qquad (14)[3]$$

---

[3]If the solution containing the iron system and that containing the hydrogen system were mixed the two systems would react either toward the right or the left as expressed below.

$$H + Fe^{+++} \rightleftharpoons Fe^{++} + H^+$$

We can anticipate and say that it would be largely toward the right as written. That is, hydrogen (represented for brevity as atomic) gives up electrons to Fe^{+++}. Fe^{++} and H^+ are formed. At equilibrium in the mixture $(\epsilon)_{Fe} = (\epsilon)_H$. Hence by (6) and (7)

$$\frac{(Fe^{++}) \, (H^+)}{(Fe^{+++}) \, \sqrt{P}} = \frac{K_H}{K_{Fe}} \qquad (8)$$

If relative values of K_H and K_{Fe} could be found, the state of the equilibrium would be defined. Such relative values will appear in due course of the development.

By mixing the two solutions we obtain no external work of definite magnitude.

Next suppose the solution containing the iron system were separated from the solution containing the hydrogen system by an intervening solution of KCl (saturated). We shall assume that this solution eliminates liquid junction potential of the kind caused by *unequal rates of diffusion* of ions. We have already anticipated the conclusion that the electron escaping tendency or activity is greater for the electrons in the hydrogen system than for those in the iron system. Presumably then electrons could escape into the potassium chloride solution from the side of the hydrogen system more easily than from the side of the iron system. But if we permit *free diffusion* of ions this should cause no potential difference since the electrons can be accompanied by positive ions, and since we have postulated for the sake of simplicity that the KCl-solution eliminates diffusion potentials of the ordinary kind. Indeed there is no occasion to

E of (13) is here written $\mathbf{E_h}$ to signify reference to the standard hydrogen system. When $(Fe^{++}) = (Fe^{+++})$, $\mathbf{E_h} = \mathbf{E_{Fe}}$.

In general when $(\epsilon)_H$ is unity and the hydrogen system is connected as specified with any oxidation-reduction system the electron activity of which is (ϵ), equation (9) may be written as (15)

$$\mathbf{E_h} = -\frac{\mathrm{RT}}{\mathbf{F}}\, ln\,(\epsilon) \qquad\qquad (15)$$

This will be our "fundamental" equation.   See footnotes 3 and 4.

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believe that there occurs appreciable transfer of free electrons across the the boundary. Of course, in time, the components of the iron and hydrogen systems will diffuse, meet and interact. But we shall assume that this does not occur within the time of an ordinary experiment. For ordinary purposes we can assume that the interposed solution of KCl is itself "unattacked" and keeps the two oxidation-reduction systems from interacting.

But suppose that the intervening KCl-solution contained some oxidation-reduction system which could be acted upon by the iron system on the one hand, or by the hydrogen system on the other hand, or by both. If we permit diffusion of the components of this new system within the intervening solution, or assume transfer of electrons in the tendency of the intermediate system to maintain equilibrium between contiguous layers, it is obvious that the new system will transmit to the iron system the reducing action of the hydrogen system or that it will transmit to the hydrogen system the oxidizing action of the iron system. Then, in the iron solution, the concentration of Fe^{+++} will be lowered and that of Fe^{++} raised; while, in the hydrogen system under constant hydrogen pressure, the concentration of H^+ will be raised. To compensate for these effects negative ions must migrate from the iron side to the hydrogen side and in quantity equivalent to the virtual flow of electrons in the opposite direction. Consequently no unidirectional electric current has been produced. No external work of definite magnitude is produced.

In passing it may be emphasized that we are assuming both free movement of ions and simultaneity of events. In the absence of either of these conditions interesting phenomena might occur.

Return to the case in which the iron- and the hydrogen systems are separated by the pure solution of potassium chloride. But now provide *any new path* by which electrons *unaccompanied by ions* can pass from the side where their escaping tendency is the higher to the side where their escaping tendency is the lower. Filter the ions, as it were. Continuing with our anticipation which is to be fulfilled when the formulation is complete and the data are at hand, we state that the electron escaping tendency is the greater at the hydrogen side. Therefore, through the path

In general an oxidation-reduction system can be defined by

$$Ox + n\epsilon \rightleftharpoons Red^{n-}$$

by

$$Ox^{n+} + n\epsilon = Red$$

or by any intermediate case. To avoid complexity of symbols consider the first of the above cases to be the type and write the equilibrium equation

$$(\epsilon) = \sqrt[n]{K \frac{Red^{n-}}{Ox}} \qquad (16)$$

Substitute the equivalent of (ϵ) by equation (16) in equation (15) and separate the constant as E_o.

$$E_h = E_o - \frac{RT}{nF} \, ln \, \frac{(Red^{n-})}{(Ox)} \qquad (17)$$

This is the type equation for the electromotive force between any oxidation-reduction system (involving **n** equivalents in a non-stepwise oxidation or reduction) and the standard hydrogen system connected in the manner indicated.

The procedure provides a uniform method of deriving the electromotive force equation for any oxidation-reduction system referred to the hydrogen standard.

In the development given above we have not specified the

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provided, electrons will pass from the hydrogen side leaving an excess of H^+ on that side. They will enter the iron system and transform Fe^{+++} to Fe^{++}. Excess chloride ions are left on the iron side. These migrate to the excess H^+ on the hydrogen side. A unidirectional electric current is generated. Simultaneity of the steps, separated for purposes of description, is, of course, assumed.

Were these processes allowed to take place without restraint there would be waste of energy by resistance, heating, etc. But now let the electron path be supplied with any device whereby the pressure of the electron stream can be exactly counterbalanced. Presumably, if the whole system is under constant external pressure and constant temperature, and if the pressure of the electrons is balanced, we have the conditions for the measurement of the free energy change of a reversible process.

nature of the path[4] whereby electrons *without accompanying ions* may pass from one oxidation-reduction system to another.

The path usually provided, although not necessarily the only path that could be provided, is a metallic path. In providing such a path we feel fairly sure that appreciable transfer of ions does not occur and that movement of electrons, or the equivalent thereof, does occur in that path.

However, if our formulation is to hold there should be no appreciable attack upon the metal immersed in either solution. Were that to occur there would be a local effect comparable with the local effect in the case of direct contact between the iron and

[4] That the Volta-effect does not enter is indicated as follows: Let ∂F be the increase in total free energy of a system when ∂n equivalents of electrons are added. Then $\dfrac{\partial F}{\partial n}$ is the partial molar free energy of electrons in that system.

When an electron is removed from a material system an unmatched positive charge is left. There is then an electrostatic attraction which must be overcome. This electrostatic effect is part of $\dfrac{\partial F}{\partial n}$. Therefore, $\dfrac{\partial F}{\partial n}$ will be considered to be made up of two terms. One of these, F, corresponds to the free energy of neutral molecules. The other is the electrostatic energy, $N_0 \epsilon V$ where V is the electrostatic potential, N_0 is the Avogadro number and ϵ the electron charge (negative).

$$\frac{\partial F}{\partial n} = F - N_0 \epsilon V \qquad (a)$$

Assume two metals indicated in the following equations by subscripts m_1 and m_2 and two solutions indicated by subscripts s_1 and s_2.

Let metal m_1 be contiguous to solution s_1 and metal m_2 be contiguous to solution s_2. At these contiguous faces interchanges of electrons or material permit establishment of equilibrium between the contiguous phases.

Hence

$$\frac{\partial F_{m_1}}{\partial n} = \frac{\partial F_{s_1}}{\partial n} = F_{m_1} - N_0 \epsilon V_{m_1} = F_{s_1} - N_0 \epsilon V_{s_1} \qquad (b)$$

Also

$$\frac{\partial F_{m_2}}{\partial n} = \frac{\partial F_{s_2}}{\partial n} = F_{m_2} - N_0 \epsilon V_{m_2} = F_{s_2} - N_0 \epsilon V_{s_2} \qquad (c)$$

hydrogen systems discussed in footnote 3.   To avoid the latter we separated the two solutions by "unattackable" KCl-solution.   To avoid the similar effect at the electrode we provide an "unattackable" metal.

A base metal in contact with a solution of its ions is a very special and a *comparatively* rare case, although it is the case which, until recently, has received the most attention.   Certain aspects of this case can be discussed to better advantage later. For the moment we may assume that the massive metal maintains the activity of the metal molecules or atoms in the given solution at a constant value.   Therefore, the equilibrium equation (18) of the system

$$M^{n+} + n\epsilon \rightleftharpoons M$$

$$(\epsilon) = \sqrt[n]{K_m \frac{(M)}{(M^+)}} \tag{18}$$

may be written

$$(\epsilon) = \sqrt[n]{\frac{K_{sm}}{(M^{n+})}} \tag{19}$$

In accordance with the scheme discussed above, solutions s_1 and s_2 are to be separated by an "unattackable" solution to prevent transfers which will establish a mixing.   But for present purposes we can neglect the intermediate solution and retain the conditions it was supposed to establish.   One of these was elimination of junction potential due to unequal migration of ions.   Another was such an unrestrained migration of ions as to prevent the production of any excess electric charge of any kind in either solution.   In short, it is supposed that no electrostatic difference of potential exists between the two solutions.   Therefore,

$$V_{s_1} - V_{s_2} = 0 \tag{d}$$

By (b) (c) and (d)

$$\frac{\partial F_{m_1}}{\partial n} - \frac{\partial F_{m_2}}{\partial n} = F_{s_1} - F_{s_2}$$

But it is the difference in free energy per equivalent of electrons which is measured by the potentiometric method, and it is the difference $F_{s_1} - F_{s_2}$ that was used in our formal equations.

For references on the Volta-effect see Rodebush (1927), Langmuir (1916), Lodge (1885) and Corbino (1927).

By the usual procedure we substitute the equivalent of (ϵ) by (19) in the "fundamental equation," (15). We also separate the constant as usual and obtain:

$$E_h = E_o + \frac{RT}{nF} \; ln \; (M^{n+}) \tag{20}$$

For convenience we shall now assemble a few equations of particular importance to our subject.

The "hydrogen system":

$$E_h = - \; \frac{RT}{F} \; ln \; \frac{\sqrt{P}}{(H^+)} \tag{21}$$

The "oxygen system":

$$O_2 + 2H_2O + 4\epsilon \rightleftharpoons 4OH^-$$

Let (H_2O) be constant. p_o = pressure of O_2.

$$E_h = E_o - \frac{RT}{F} \; ln \; \frac{(OH^-)}{\sqrt[4]{p_o}} \tag{22}$$

Metal-metal ion system:

$$M^{n+} + n\epsilon \rightleftharpoons M$$
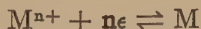
See above

$$E_h = E_o + \frac{RT}{nF} \; ln \; (M^{n+}) \tag{23}$$

Any oxidation-reduction system of the type

$$Ox + n\epsilon \rightleftharpoons Red^{n-}$$
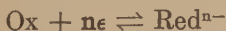
$$E_h = E_o - \frac{RT}{nF} \; ln \; \frac{(Red^{n-})}{(Ox)} \tag{24}$$

Special oxidation-reduction system

$$Ox + 2\epsilon \rightleftharpoons Red^{--}$$

$$E_h = E_o - \frac{RT}{2F} \; ln \; \frac{(Red^{--})}{(Ox)} \tag{25}$$

The development given above may not be comprehensive enough to meet all requirements as to detail but it is general enough and sufficiently rigid to have some advantage. Its chief advantages are: first an easily remembered device for the formulation of the orienting equation of any cell, second the emphasis of the family relationship of cells which all too often are considered unique. Both of these advantages will be utilized in the discussion of important matters to follow.

THE PARTICIPATION OF HYDRIONS

Of importance to the subject of this book is the fact that the reductant appearing in equation (25) is an anion. There are various cases analogous with this but different in type. For instance, a positive charge in an oxidant's cation may be neutralized by one electron and an anion may be created by a second electron.

$$Ox^+ + 2\epsilon \rightleftharpoons Red^-$$
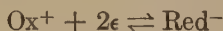
It will not alter the principle if we continue with the very simple case described by

$$Ox + 2\epsilon = Red^{--}$$
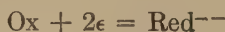
The orienting electrode equation is

$$E_h = E - \frac{RT}{2F} \ln \frac{(Red^{--})}{(Ox)} \qquad (26)$$

And now to avoid complexities, the consideration of which would not seriously alter the conclusions, we shall assume that activities may be replaced by concentrations. Equation (26) then becomes:[5]

$$E_h = E - \frac{RT}{2F} \ln \frac{[Red^{--}]}{[Ox]} \qquad (27)$$

Assume that the oxidant has neither acidic nor basic groups and that its concentration during shifts in hydrion concentration can always be identified as that of the total oxidant, $[S_o]$. If we wish to reconstruct (27) to include the total reductant, $[S_R]$, as is

[5] In this book () signifies activity and [ ] concentration.

necessary when we know nothing about the concentration of the anion, Red^{--}, and are forced to measure the total reductant, it is necessary to use the equilibrium equations:

$$\frac{[H^+]\,[HRed^-]}{[H_2Red]} = K_1 \tag{28}$$

$$\frac{[H^+]\,[Red^{--}]}{[H\ Red^-]} = K_2 \tag{29}$$

and the summation

$$[S_R] = [Red^{--}] + [H\ Red^-] + [H_2Red] \tag{30}$$

Substitute (28) and (29) in (30) and solve for $[Red^{--}]$

$$[Red^{--}] = \frac{[S_R]\,K_1\,K_2}{K_1\,K_2 + K_1\,[H^+] + [H^+]^2} \tag{31}$$

Substitute (31) in (27), collect constants under E_o and replace $[Ox]$ by $[S_o]$.

$$E_h = E_o - \frac{RT}{2F}\,ln\,\frac{[S_R]}{[S_o]} + \frac{RT}{2F}\,ln\,[K_1\,K_2 + K_1\,[H^+] + [H^+]^2] \tag{32}$$

If $[H^+]$ is kept constant, as by means of a strong buffer solution, the last term of (32) is constant and (32) may be written:

$$E_h = E_o' - \frac{RT}{2F}\,ln\,\frac{[S_R]}{[S_o]} \tag{33}$$

It was this equation that was used in constructing the curves of figure 73.

When the acidic or basic nature of the system is changed, the form of the last term in equation (32) is altered. For the system

$$\overset{+}{Ox} + 2\epsilon \rightleftharpoons Red^-$$
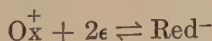
$$E_h = E_o - \frac{RT}{2F}\,ln\,\frac{[S_R]}{[S_o]} + \frac{RT}{2F}\,ln\,\frac{K_r\,[H^+] + [H^+]^2}{K_o\,[H^+] + K_w} \tag{34}$$

where K_r is defined by

$$K_r = \frac{[Red^-]\,[H^+]}{[H\ Red]}$$

and K_o is defined by

$$K_o = \frac{[O_x^+]\, K_w}{[OxOH]\,[H^+]}$$

Thus it is evident that the peculiarities of a given system are (with some exceptions) expressed by the last term of such equations as (32) and (34).

Obviously if $[H^+]$ is constant, (34) like (32) may be written as (33).

To study the last term of (32) set $\dfrac{[S_R]}{[S_o]} = \dfrac{1}{1}$. Then (32) becomes (35)

$$E_h = E_o + \frac{RT}{2F}\, ln\, [K_1 K_2 + K_1\,[H^+] + [H^+]^2] \qquad (35)$$

The geometry of (35) is illustrated in figure 74. Vary $[H^+]$ but let $[H^+]$ be determined in each instance by the independently measured pH value of a buffer solution. When $[H^+]$ is large in relation to K_1 and K_2, E_h varies as $\dfrac{RT}{F}\, ln\, [H^+]$, or, at 30°, -0.06 pH. When $[H^+]$ is small in relation to K_1 and K_2 the last term in (35) is practically constant and the potential is no longer affected by alteration of pH. Between these extremes the curve passes through points of inflexion centered at values of pH equal to pK_1 and pK_2.

In figure 74 the geometry of (33) is illustrated by the curves for certain fixed values of $[H^+]$. Left of figure.

To obtain the picture representative of the complete equation (32), a figure in three dimensions is necessary. It will be similar to that represented by the isometric drawing of figure 75. This shows a surface descriptive of the system of which 2–6 dibromo benzenone indophenol is the oxidant. (See Cohen, Gibbs and Clark (1924).)

In many cases which have proved amenable to measurement, other than the two acidic groups assumed above for purposes of simplicity must be taken into consideration. Even a group not directly concerned in the oxidation-reduction process may have its dissociation constant altered when the substance is transformed

from an oxidant to a reductant.   The resulting energy-change then
becomes evident; and the equation required to account for the
actual measurements may be more complicated.

The more varied examples of the several effects are to be found
in a series of papers entitled *Studies on Oxidation-Reduction* by
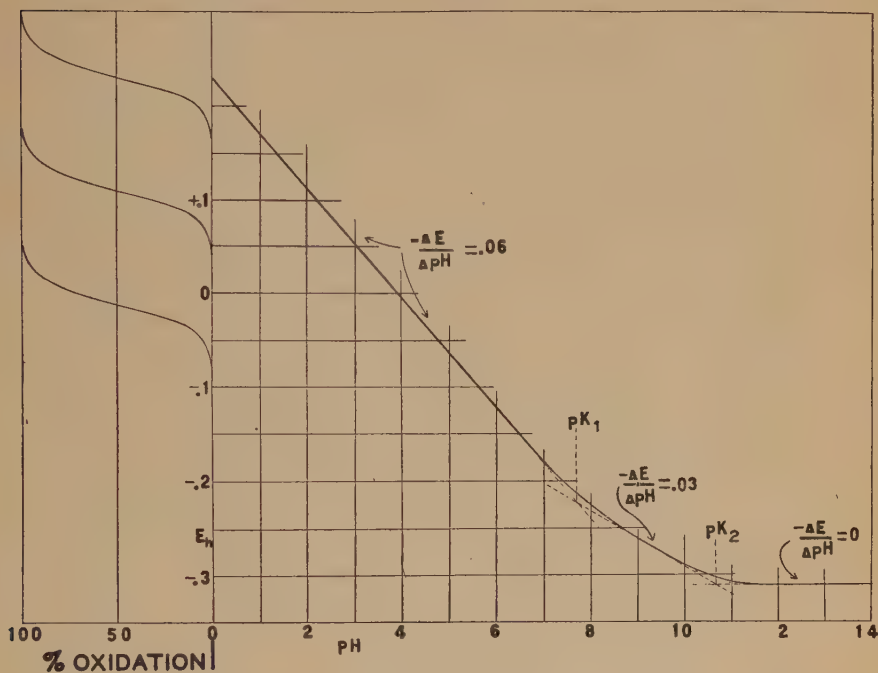
Fig. 74. (*Left*) Relation of Electrode Potential to Percentage
Oxidation at Constant pH at Various Levels of pH; (*Right*)
Relation of Electrode Potential to pH at Constant Percentage
(50 per cent) Oxidation

System: Anthraquinone,2,7-disulfonic acid and its reductant at 25°.

Drawn from data of Conant, Kahn, Fieser and Kurtz (1922). $\dfrac{-\Delta E}{\Delta pH} =$

0.05912 expressed as 0.06.

Clark, Cohen, Gibbs, Sullivan, Cannan *et al.* reviewed up to 1925
by Clark in *Chemical Reviews, 2*, 127, (1925).   See also the ref-
erences there given to papers by Biilmann, by LaMer, by Conant
and their coworkers.

Since, in the majority of cases, equation (33) applies when $[H^+]$ is constant, this equation may be considered applicable at any fixed level of $[H^+]$ and attention may be centered upon the relation of potential to pH when $\dfrac{[S_R]}{[S_o]} = 1$. With this understood a
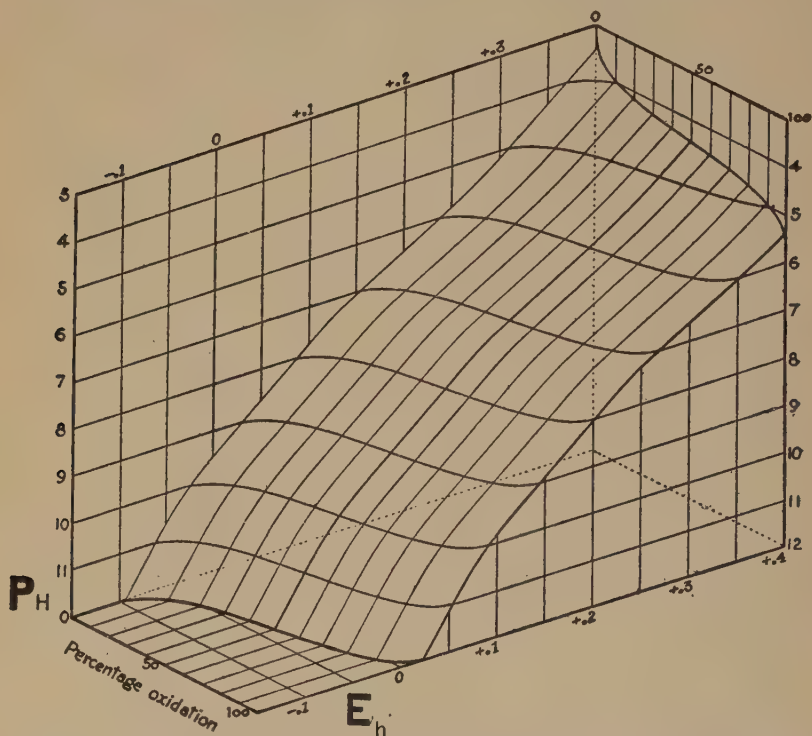
FIG. 75. ISOMETRIC DRAWING OF THE SURFACE DESCRIPTIVE OF THE SYSTEM COMPOSED OF 2-6 DIBROMO PHENOL INDOPHENOL AND ITS REDUCTANT

(After Cohen, Gibbs and Clark (1924). See Clark *et al.* Studies on Oxidation-Reduction, VI.)

system may be described graphically by the so-called E'_o: pH curve. Figure 76 illustrates a few of the many cases in which $\dfrac{[S_R]}{[S_o]}$ has been maintained at a ratio of unity and the potential measured as pH is varied. On curves 3 and 4 (fig. 76) the points at pH = 3.91 correspond to the mid-points of the corresponding curves in figure 73.
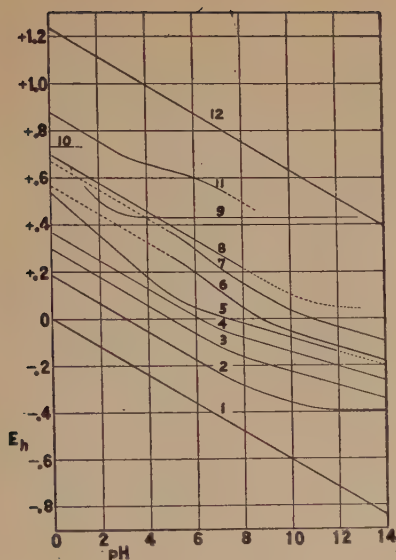
Fig. 76

Fig. 77

Fig. 76
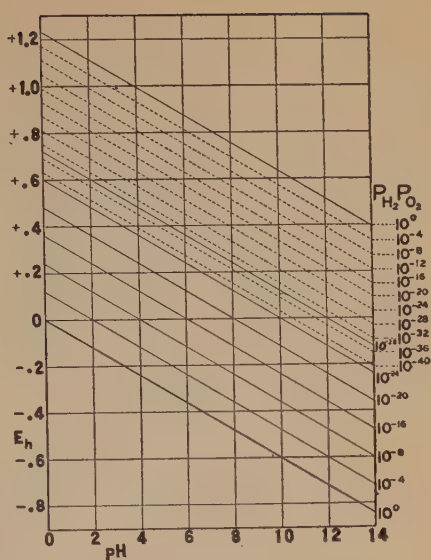
1. Relation of potential of hydrogen electrode (1 atmosphere H_2) to pH.
12. Theoretical relation of potential of oxygen electrode (1 atmosphere O_2) to pH.
2–11. Systems at 50 per cent reduction, named below by one component.
2. Anthraquinone-β-sulfonic acid (oxidant).
3. Indigo disulfonate (oxidant).
4. Indigo tetra sulfonate (oxidant).
5. Methylene blue (oxidant).
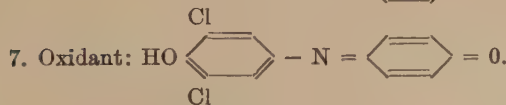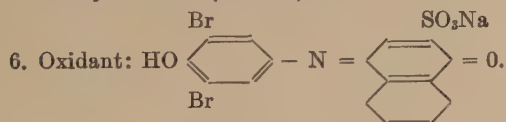
6. Oxidant:

7. Oxidant:

8. Benzo-quinone (oxidant).
9. $K_3Fe(CN)_6 : K_4Fe(CN)_6$.
10. $Fe^{+++} : Fe^{++}$.
11. o-Tolidine (reductant).

Fig. 77. Theoretical Relations between Electrode Potential, Eh, pH and Partial Pressures of Hydrogen and Oxygen

Each decrement of the partial pressure of hydrogen by 10^{-4} shifts the potential of a hydrogen electrode at $30° + 0.03 \times 4 = 0.12$ volt.

Each decrement of the partial pressure of oxygen by 10^{-4} shifts the theoretical potential of an oxygen electrode $- 0.015 \times 4 = -0.06$ volt.

Since the position of any one of the diagonals of figure 77 is determined by log $\frac{1}{\text{hydrogen pressure}}$, Clark proposed the term "rH" for this quantity, believing that it would be a convenience for the general discussion of the general position of an oxidation-reduction system. Unfortunately the term rH has been frequently used where potential would be far preferable. Because of this indiscriminant use, further employment of rH is to be discouraged.

THE RELATION OF HYDROGEN POTENTIALS TO GENERAL RELATIONS
DESCRIBED GRAPHICALLY

To show graphically the possibilities of interpreting the potentials of one system in terms of the potentials of another consider figure 77. At pH = 0 a properly prepared electrode under one atmosphere of hydrogen is given the arbitrary reference potential of 0. As pH increases, the potential of such an electrode becomes more negative, and, at the temperature chosen for purposes of the drawing, it becomes more negative by 0.06 volt per unit increase of pH. In short the line thus defined, and readily identified on the chart, is the line of the potential of a hydrogen electrode under one atmosphere of hydrogen. Above this line and distant about 1.23 volts at all values of pH is the line of the hypothetical oxygen electrode under one atmosphere of oxygen. The region above this line of the oxygen electrode may be considered for present purposes as the region of oxygen "overvoltage" and the region below the line of the hydrogen electrode may be considered the region of hydrogen "overvoltage." In other words they are regions in which the potentials would be such that, at the given pH value of the solution, hydrogen or oxygen, as the case might be, would be liberated from water at an equilibrium pressure of over one atmosphere. Between these arbitrary limits lie the oxidation-reduction systems which are stable enough in the presence of water not to decompose this solvent extensively.

If the hydrogen electrode be under a partial pressure of hydrogen less than one atmosphere, but constant, the line will be shifted upward (calculation by equation (21)). The successive positions of the shifted lines in the figure are determined by hydrogen pressures each of which is 1/10,000 that of the preceding.

In a similar manner there is illustrated the shift in the position of the line of the oxygen electrode as the oxygen pressure declines in steps of 1/10,000 the pressure of the preceding case. (Calculation by equation (22).)

By superimposing figure 76 on figure 77 it is possible to make a formalistic interpretation of the potentials of the various systems in terms of the potential of either an oxygen or a hydrogen electrode.

It has already been indicated that such an interpretation may be highly artificial.

Now each curve in figure 76 is for the half-reduced state of the actual system. If the potential becomes more negative, the percentage reduction of a given system increases as shown, for instance, by figure 73. To attain true equilibrium at the hydrogen electrode the methylene blue system, for instance, would first have to be "completely" reduced. To attain true equilibrium at a definite one to one ratio of methylene blue and methylene white both hydrogen and oxygen would have to be practically eliminated.

The reader himself can carry forward the further interrelationships and might profitably consider the interpretation of any electrode potential in terms of any one of the systems. He might assume, for instance, the universal presence of iron ($E_o = 0.75$) and interpret all potentials in terms of the system $Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$.

The practical aspect of the matter is this. We cannot avoid the *possibility* of other systems participating when we set up an experiment on one. Thus with a platinum electrode immersed in a mixture of ferric and ferrous ions in aqueous solution, we must, strictly speaking, consider the following oxidation-reduction systems: $Fe^{+++}:Fe^{++}$; $H^+:H_2$; $O_2:OH^-$; and $Pt^{++++}:Pt$. However, when we come to know the quantitative values of the equilibrium potentials for different systems, or even their orders of magnitude, we come to realize that the ferric-ferrous system by interaction with water or water constituents or with chloride ions in a ferrous-ferric chloride mixture cannot liberate appreciable quantities of hydrogen, oxygen or chlorine and that the potential of the system is incompatible with appreciable amounts of platinum ions. No appreciable energy flows into the transformation of these systems and we rest content that we are concerned practically with only the energy changes of the system $Fe^{++}:Fe^{+++}$.

In general, characteristic data for one system should be obtained under conditions which preclude interference by another system.

This is the conclusion we anticipated during the formulation in the first instance. The quantitative data of accuracy suffi-

cient for the purpose may be found in the compilation by Abegg, Auerbach and Luther (1911–1915). *Cf.* Gerke (1925).

USE OF THE GENERAL RELATIONS IN DETERMINING pH VALUES

Suppose the potential of an electrode were stabilized by some definite oxidation-reduction system which involved the hydrion. As one instance consider a system to which there applies the equation

$$\mathbf{E_h} = \mathbf{E_o} - \frac{RT}{2F} \, ln \, \frac{[S_R]}{[S_o]} + \frac{RT}{2F} \, ln \, [K_1 K_2 + K_1 [H^+] + [H^+]^2] \quad (36)$$

If there were no interaction of oxidant or reductant with constituents of the solution, the addition of the oxidant and reductant in a one to one ratio would leave

$$\mathbf{E_h} = \mathbf{E_o} + \frac{RT}{2F} \, ln \, [K_1 K_2 + K_1 [H^+] + [H^+]^2] \quad (37)$$

If K_1 and K_2 were very small in relation to $[H^+]$ it would mean that, while this relation held, the acidic nature of the reductant would not be brought into play to affect the acid-base equilibrium of the solution. Also the above equation would then reduce to

$$\mathbf{E_h} = \mathbf{E_o} + \frac{RT}{F} \, ln \, [H^+] \quad (38)$$

If we may assume that $\mathbf{E_o}$ has been evaluated by a set of standardizing measurements with known values of $[H^+]$, then in any other case a determination of $\mathbf{E_h}$ yields the value of $[H^+]$.

Chapter XIX will be devoted to such cases.

There remains a possibility not yet given the attention it deserves.

It was specified above that the oxidant or reductant should not react with other reductants or oxidants in the solution and thus suffer a change in ratio. This is a severe limitation, which, as we shall see in a later chapter, appears less prominently in practice than might be expected because of the slowness of certain oxidation-reduction processes. If the potential-controlling system were to suffer oxidation or reduction, there would be a change of

potential independent of a change in pH. In many cases this means that protection from the oxidizing action of the air would have to be provided. In all cases it means avoidance of the presence of any oxidizing or reducing agent sufficiently active to appreciably attack, within the time of the experiment, either the reductant or the oxidant employed. This does not mean that *any* oxidizing or *any* reducing agent is an incompatible. Quite the contrary will reveal the still unutilized possibilities in determining the dissociation constants of very active oxidants and reductants.

Assume for instance that the system designated by $Ox_a : Red_a$ is to be employed in equimolecular mixture. Suppose that the potential of this system varies linearly with pH. Now let it be applied to the measurement of the pH values of solutions containing the reductant of a system designated by $Red_b : Ox_b$.

Were the characteristic potential of the "b" system negative to that of the "a" system, there would be extensive interaction between the "a" and "b" systems. The reductant of the "b" system would reduce some of the oxidant of the "a" system. The extent is determined by the relative concentrations and also by the "spread" between the "characteristic" potentials of the two systems.

But were the potential of the "b" system *positive* to that of the "a" system the *reductant* of the "b" system could *not* act extensively upon the *oxidant* of the "a" system. Therefore, if the "b" system were used in an extensively reduced condition (practically the reductant alone), the ratio of oxidant to reductant in the "a" system should not be seriously affected.

How seriously remains to be calculated by specific assumptions.

At constant pH the potentials of the systems separately are defined by

$$E_{ha} = E_a' - 0.03 \log \frac{[Sr_a]}{[So_a]} \tag{39}$$

$$E_{hb} = E_b' - 0.03 \log \frac{[Sr_b]}{[So_b]} \tag{40}$$

The systems react to a common potential, $E_{ha} = E_{hb}$. Hence:

$$E_a' - E_b' = 0.03 \log \frac{[Sr_a][So_b]}{[So_a][Sr_b]} \tag{41}$$

Let $E'_a = 0.15$ volt and $E'_b = 0.60$ volt.

Then

$$\frac{[Sr_a][So_b]}{[So_a][Sr_b]} = 10^{-15} \qquad (42)$$

Let the initial concentrations of the measuring system be as low as $[Sr_a] = [So_a] = 10^{-4}$ while of the measured system let $[Sr_b]$ be as high as 1 normal, initially. In changing from the initial state to that defined by (42) x moles of reductant "b" have reacted with x moles of oxidant "a" to increase by x moles the concentration of reductant "a" and form x moles of oxidant "b."[6]

$$\frac{[10^{-4} + x][x]}{[10^{-4} - x][1 - x]} = 10^{-15}$$

An approximate solution of this yields a value of x very nearly zero. In other words the measuring system, "a," has not been appreciably affected.

This principle is tacitly assumed in the application of the hydrogen: hydrion system to the measurement of pH values in solution containing a reductant of another oxidation-reduction system; but the principle should be applicable generally, and not only to measurements in the presence of reductants, but also to measurements in the presence of oxidants. In the latter case the measuring system should be one as positive as can be selected.

It is to be hoped that when a sufficient variety of well defined systems are available the principle here described will be applied and will leave no excuse for an ionization constant of any oxidant or reductant remaining undetermined when its value is of appreciable magnitude.

For an example see Cannan and Knight (1928).

ON THE SIGN OF "ELECTRODE POTENTIALS"

On page 375 the electromotive force of a cell is formulated by use of the postulate that the escaping tendencies or activities of the electrons are different in two oxidation-reduction systems. In the cell these two oxidation-reduction systems are placed in

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[6] For simplicity there are assumed equivalent valences.

liquid junction with an intermediate solution which can be attacked chemically by neither oxidation-reduction system but which will permit migration of ions. We assume, for simplicity, equality of ionic migrations and, therefore, no potential difference at the junction. The metallic circuit provides a path which permits electrons but not ions to migrate from one system to the other.

The introduction of a path through which electrons alone pass from the one system to the other establishes a unidirectional electric current. If the current is not entirely restrained it will appear that this path (usually a metal) has the more negative potential in the section nearest the system of higher electron escaping tendency.

With this scheme it becomes a convenience to give to the potential of an electrode the sign of the **metal** as found in a cell made up of the given electrode and the standard of reference, the normal hydrogen electrode.

This is, I am told, in harmony with the convention to be used in *International Critical Tables*.

In relating a cell reaction to the signs of the cell terminals it is convenient to argue as follows.

The *system* $Cl_2 : Cl^-$ has a much greater tendency to absorb electrons (oxidize) than has the *system* $H_2 : H^+$ (which is the reducing system *par excellence*. An indifferent electrode may be thought of as an indicator of the relative ability of the solution system to give or take electrons. It is charged positively by an oxidizing *system* such as $Cl_2 : Cl^-$, relative to the charge produced by a reducing *system* such as $H_2 : H^+$. The extension of the concept is simple. It must, of course, be combined with some convention regarding the way of writing the cell reaction in cases which are not obvious.

When a cell description is written in this book, it will be written not only with the relatively negative metal phase at the *left*, but, to avoid any ambiguity, each sign will be given as that of the exterior lead on open circuit, the open circuit being the ideal potentiometric balance as if against a condenser. Thus

$$- \text{Pt, } H_2 \mid \text{HCl, HgCl} \mid \text{Hg } +$$

means that the mercury is positive relative to the platinum as it would be found to be at potentiometric balance. The reductant

(H_2) of the system having the higher electron escaping tendency releases electrons to the nearest metal. These electrons flow in the exterior circuit to attack the oxidant and set free the reductant (Hg) of the system with the lesser electron escaping tendency.

Lewis and Randall in *Thermodynamics* adopt "the convention that the electromotive force given shall represent the tendency of the negative current to pass spontaneously through the cell from right to left." (*Thermodynamics*, p. 390.)

They write

$$H_2(g), HCl (0.1 M), Cl_2(g); E = 1.4885$$

or

$$Cl_2(g), HCl (0.1 M), H_2(g): E = -1.4885$$
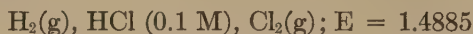
When they represent a half-cell such as

$$Hg \mid HgCl, KCl (0.1 N) \parallel$$

they state the order electrode | electrolyte. "We then say that the single potential measures the tendency for negative electricity to pass from right to left." When they write

$$\text{"D.E.}; E = -0.3351\text{"}$$

they refer the potential of the "decinormal electrode" to the normal hydrogen electrode by

$$Hg \mid HgCl, KCl (0.1 N) \parallel H^+ \text{ (activity 1)} \mid H_2 \text{ (1 atmos.) Pt}$$
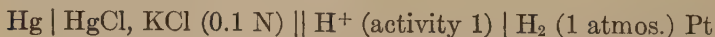
and, since the negative current goes from left to right through the cell as written, the negative sign is given, as above.

As a consequence it is found that the signs given to single electrode potentials by Lewis and Randall, and by many who adopt their convention, are opposite to those used in this book.

We could use the system of Lewis and Randall by writing, for instance,

$$\parallel KCl (0.1 N), HgCl \mid Hg; E = 0.3351$$

instead of their

$$Hg \mid HgCl, KCl (0.1 N) \parallel ; E = -0.3351$$

Although this will frequently be done we here ignore the order and use the following convention. The sign of an electrode

potential of a given half-cell shall be the sign of the potential of its metal relative to that of the metal of the normal hydrogen half-cell.

For interesting discussions of the sign of electrode potentials see: Lewis and Randall (1923), Porter (1924) and *Transactions American Electrochemical Society* **31,** 249; **33,** 85; **34,** 196.

ON FINITE RATIOS

In any case where a definite potential difference is to be established at the electrode there must be in the system two species, one of which is the direct or indirect reduction product of the other, and the ratio of their concentrations or activities must be of finite magnitude. Neglect of this principle is not infrequent, and is doubtless due to the emphasis which has been placed upon the final, working-form of the equation for the difference of potential between a metal and a solution of its ions. See equation (20) page 381. In obtaining the final form of this equation certain assumptions have been made and the potential-difference at the electrode is made to appear as if it were dependent only upon the concentration of one species, namely the metal ions. Whether this be the explanation or not, there are not infrequently encountered in the literature attempts to measure electrode potential differences with a single oxidant or reductant. It should be plain from a study of figure 73 that, when the oxidant or reductant alone is present, the electrode potential-difference becomes asymptotic to the E_h axis. Were it possible to eliminate absolutely every trace of the oxidant, the potential-difference obtained with the reductant alone would *tend* to become infinite.

When we meet such a prediction in an equation we should be suspicious. Perhaps for the potential produced by a pure reductant or by a pure oxidant there is an inherent limitation of a kind not implied by the equation which rests upon the assumption of a reversible system. On the other hand the general treatment implies the following.

The potential could not become infinite for two reasons. In solution an infinitesimal reaction with the solvent would prevent it. Second the production of a pure reductant could not be attained in a world which has suffered extensive interactions of its components unless there were created *de novo* another reducing reagent belonging to a system of infinite negative potential or unless there were created *de novo* an absolutely pure reducing agent which could be the reductant of a low potential system if it were employed in infinite mass.

Wherever stable potentials are reported as having been found with reductant alone it is doubtless due to the presence of the oxidant as an impurity.

While there may be no rigid proof of the statements made above they are implicit in the equations. Whatever their limitations, they have several *practical* implications.

So far as mere formulation is concerned it should be possible to attain the electrode potential of the system metal-metal ion by means of an unattackable metal immersed in a solution of the metal ions, provided the saturation value of the metal were maintained by a piece of the metal placed elsewhere. The system metal-metal ion is a special case of an oxidation-reduction system which should be measurable in the ordinary way. The difficulty would be in maintaining between the metal serving merely as electrode and the metal serving merely as saturator a sufficiently fast diffusion of the almost insoluble metal molecules to maintain a finite ratio of oxidant to reductant at the electrode. For this reason the only practical way is to make the electrode of the metal itself or to have it present at the electrode in appreciable quantities, as in the case of an amalgam electrode. Otherwise the *inevitable impurities*, such as hydrogen or oxygen, of the "unattackable" electrode would make it behave as a more or less indefinite hydrogen, oxygen or other kind of electrode.

By the same token a system which does not reversibly maintain a finite ratio of oxidant and reductant, leaves the electrode functioning in an *almost uninterpretable* manner. Irrespective of what can be done under such circumstances, the recognition of this fact leads to skepticism regarding all measurements which cannot satisfy the requirements of the equations on introduction of known components. There is ample room and frequent occasion for bold adventure in the use of electrode measurements, especially in the study of so-called irreversible, organic oxidation-reduction systems; but, unless the equations can be satisfied by the introduction of known components, one should warn his reader that he is adventuring and that he is not citing definitive data.

FREE ENERGY CHANGES

Since the validity of Faraday's law is assumed and measurements of cells are measurements of electromotive force, it has been convenient to separate E_h and to place nF on the other side of the equation. However, nFE is the free-energy change in volt-coulombs. Therefore, all the electromotive force equations permit the calculation of the free energy-change, $-\Delta F$, from

$$-\Delta F = nFE \qquad (43)$$

It is unnecessary to repeat all the equations in the new form; but one case will be instructive. Consider equation (32) page 383 and rewrite it as:

$$-\Delta F = 2FE_h = 2FE_o - RT\, ln\, \frac{[S_R]}{[S_o]} + RT\, ln\, [K_1K_2 + K_1\,[H^+] + [H^+]^2] \quad (44)$$

The employment of E_h signifies (by subscript h) reference to the "normal hydrogen electrode." For simplicity we shall consider this to be a hydrogen electrode in a solution of unit hydrion *concentration* under one atmosphere pressure of H_2. Therefore, the processes to be discussed involve reference to this standard hydrogen system.

We shall assume that K_1 and K_2 have such values that $[H^+]$ can be made either large or small with relation to either.

Let it be assumed in all cases that $[S_R] = [S_o] = 1$. Then equation (44) can be written

$$-\Delta F = 2FE_o + RT \ln [K_1 K_2 + K_1 [H^+] + [H^+]^2] \tag{45}$$

First make $[H^+]$ large in relation to K_1 and K_2. Then we have practically

$$-\Delta F_1 = 2FE_o + 2RT \ln [H^+] \tag{46}$$

When $[H^+] = 1$ we have

$$-\Delta F_2 = 2 \ FE_o \tag{47}$$

There is implied the suppression of the dissociation of the reductant. Hence (47) gives the free energy of the process

$$\begin{matrix} (1 \text{ atmos.}) \\ S_o + H_2 \rightleftharpoons S_R \text{ (hydrogenated)} \\ \\ Ox + H_2 \rightleftharpoons H_2 Red \end{matrix} \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\} \tag{48}$$
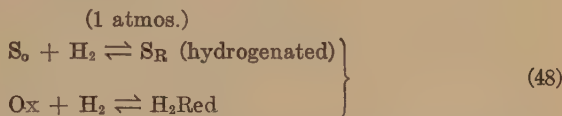
For any value of $[H^+]$ other than 1, equation (46) gives not only the free energy of the process (48) but the free energy of transport of hydrions from the standard solution to any value of $[H^+]$. See (49)

$$-\Delta F_1 + \Delta F_2 = 2RT \ln [H^+] \tag{49}$$

Second, make $[H^+]$ small in relation to K_1 and K_2. Then (45) is practically

$$-\Delta F_3 = 2FE_o + RT \ln K_1 K_2 \tag{50}$$

Subtract (47) from (50)

$$-\Delta F_3 + \Delta F_2 = RT \ln K_1 K_2 \tag{51}$$

But $K_1 K_2 = \dfrac{[H^+]^2 \ [Red^{--}]}{[H_2 Red]}$

Hence

$$-\Delta F_3 + \Delta F_2 = RT \ln \frac{[H^+]^2 [Red^{--}]}{[H_2 Red]} \tag{52}$$

Equation (52) gives the free energy of the process

$$H_2 Red \rightarrow 2H^+ + Red^{--} \tag{53}$$

This is the free energy of ionization which, by the use of $[H^+] = 1$ in the derivation, is the energy which would have to be expended to accomplish ionization against a normal concentration of hydrions. Likewise the free energy of the separate ionizations can be formulated.

When the hydrion concentration is lowered ionization takes place spontaneously. This condition is met when the free energy of hydrion transport, between 1N and the normality permitting practically complete ionization, compensates the energy which would have to be expended on the system to cause ionization at 1 N H^+.

In short, our equations contain implicitly the free energies of ionization and what may be called rather inexactly the free energy of hydrion dilution.

SOME REMARKS ON MECHANISM

It was stated early in this chapter that the use of the electron-transfer concept was to be a formality and a convenience; and, although it may have been stressed here and there in a manner which betrayed the author's preference for the concept as a *picture* of actuality, it remains a formality. The satisfaction of the resulting equations is no proof of the validity of the postulate, for it was made clear that there are several other ways in which the equations could be derived. Also the equations are of thermodynamic origin, and, although mechanistic ideas were introduced both to clarify the subject, and to make general equations specific, the fulfillment of a thermodynamic relation cannot *per se* throw any light on mechanism.

It has been repeatedly stated that the strength of thermodynamics is its independence of mechanistic concept. This is because the energy change, which a thermodynamic equation may formulate, is independent of the path. The thermodynamic method *per se* has nothing to say about conditions which might make the change take one path rather than another. Yet in this chapter we have made rather free use of certain mechanistic concepts. This is because we have to face the following situation. If free energy change is to be formulated, all that thermodynamics offers is an equation for *a* process. The methods of general chemistry must be used to give some idea of specific components to be used in the practical solution; otherwise the experimentalist is not equipped to handle the process. The innumerable methods of formulating cell reactions thermodynamically have been advanced *after* the cells have been devised.

In all cases some molecular theory is introduced. So it was that we found ourselves specifying, for instance, that a reductant can take the form H_2Red, $HRed^-$ or Red^{--}. Were the theory of electrolytic dissociation in disrepute this would be considered horribly mechanistic.

In general we find ourselves dealing with relations which take the form of the thermodynamic equation but in which we have introduced molecular theory. This introduction carries with it not only the truth of our molecular theory but its assumptions. When we put the true and the assumed into the mathematical mill the mill grinds out in new and often startling form only what is put in. Many of the consequences are very alluring and it behooves us to be on guard.

It has been shown above that whether we start with the orienting reaction

$$Ox + 2\epsilon \rightleftharpoons Red^{--}$$

or $$Ox + H_2 \rightleftharpoons H_2Red$$
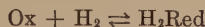
we attain the same final working equation which in this case is:

$$E_h = E_o - \frac{RT}{2F} \ln \frac{[S_R]}{[S_o]} + \frac{RT}{2F} \ln [K_1K_2 + K_1 [H^+] + [H^+]^2]$$

Let us disregard implied *electrode* mechanism and consider this last equation as an empirical one which correctly formulates experimental facts. We then *still imply* solution processes such as

$$H_2Red \rightleftharpoons H^+ + HRed^-$$

and $$HRed^- \rightleftharpoons H^+ + Red^{--}$$

In the preceding section it was shown that the equation involves the free energies of ionization and of hydrion "dilution." It, therefore, appears that a choice between the orienting reactions

$$Ox + 2\epsilon \rightleftharpoons Red^{--}$$

and $$Ox + 2\epsilon + 2H^+ \rightleftharpoons H_2Red$$

$$\left(\begin{array}{c} \text{the latter being formally equivalent to} \\ Ox + H_2 = H_2Red \end{array} \right)$$
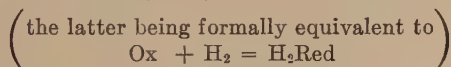
is somewhat like the choice permissible in measuring the height of a ladder. We may measure from the bottom up or from the top down. We may measure the total free energy change by counting in the free energy of ionization from one direction or the other.[7]

But suppose there is under consideration an oxidation-reduction system the reductant of which can take either the form HRed or Red⁻. While we may have properly formulated the free energy change for the formation of one or the other or both, it might well be that the species Red⁻ is effective in the electrode phenomena and that the species HRed is not effective or that HRed is effective and Red⁻ not. Now let the dissociation constant, K_a, of

$$\frac{[H^+] [Red^-]}{[H \ Red]} = K_a$$

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[7] Dixon (1927) chooses his position at the top of the ladder and leaves the impression that this has something to do with the argument of Cohen, Gibbs and Clark (1924), which, of course, it has not. See pages 402, 521 and Studies on oxidation-reduction, V. (Clark *et al.*).

have the value 10^{-13}. The ratio $\dfrac{[Red^-]}{[HRed]}$ would be 1 at pH $= 13$ while at pH $= 0$ the ratio would be 10^{-13}. A thousandth normal solution would contain the species Red$^-$ at only about 10^{-16} normality. If we choose to say that this species is the exclusively active reductant we have to account for physical effectiveness at 10^{-16} N. The discussion now joins with the remarks on page 372 concerning the assumed functioning of the electrode as a hydrogen electrode in a ferric-ferrous ion solution. We found there but one of many instances of the physically absurd values encountered when *restricted points of view and restricted methods of expressing relations* are applied to electrode potential differences. One or two other instances will be given.

Lehfeldt (1899) says of the so-called solution pressures postulated by Nernst and briefly discussed in Chapter XII:

"...... we have Zinc................................. 9.9×10^{18}
     Nickel............................... 1.3×10^{0}
     Palladium........................... 1.5×10^{-36}

The first of them is startlingly large. The third is so small as to involve the rejection of the entire molecular theory of fluids."

Lehfeldt then shows that, in order to permit at the electrode the pressure indicated above for palladium, the solution would have to be so dilute as to contain but one or two ions of palladium in a space the size of the earth. No stable potential could be measured under such a circumstance. On the other hand Lehfeldt calculates that to produce the high pressure indicated for zinc "1.27 grams of the metal would have to pass into the ionic form per square centimeter, which is obviously not the case."

Another aspect of the matter was emphasized in a lively discussion between Haber, Danneel, Bodländer and Abegg in *Zeitscrift für Elektrochemie*, 1904. Haber points out that, if the well established relation between a silver electrode and a solution containing silver ions be extrapolated to include the conditions found in a silver cyanide solution, the indicated concentration of the silver ion will be so low as to have no physical significance. Haber mentions the experiment of Bodländer and Eberlein where the potential and the quantity of solution were such that there was present at any moment less than one discrete silver ion. The greater part of the discussion centred upon the resolution of the equilibrium constant into a ratio of rates of reaction, and upon the conclusion that, if the silver ion in the cyanide solution has a concentration of the order of magnitude calculated, it must react with movements of a speed greater than that of light *or else that the known reactions of silver in silver cyanide must take place directly from the position in the complex. Previous ionization is then unnecessary.* Were the latter assumption not true, how could the stability of the electrode potential be supported?

A similar question was raised but not answered in a discussion between Langmuir and Patten printed in Trans. Am. Electrochem. Soc. *29*, (1916)

pp. 293 and 296. It concerned the hydrogen electrode operating in a solution of hydrion concentration of 10^{-10} normal. Whatever the validity of the conclusion that so and so much free energy-change is involved in the transfer of hydrions from one normal to 10^{-10} normal, is such a low concentration physically effective?

These matters may be somewhat clarified if we return to a consideration of the oxidation-reduction systems noted above.

Here are systems in the description of which there are included the free energies of complex formations, i.e., the formation of the undissociated acids or bases from their ionization products. By analogy, there should be included in the description of the silver system the free energy of formation of the silver cyanide complex. By the neglect of this aspect, the chosen, orienting reaction

$$Ag^+ + \epsilon \rightleftharpoons Ag$$
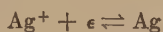
has been raised to an importance to which it is not entitled. It is because of emphasis upon this orienting reaction that there has been created the puzzle mentioned above.

But there still remains a real, mechanistic problem. The only answer that appears plausible is, as mentioned above, that the silver cyanide acts directly.

Thus Brønsted (1926), in discussing a similar situation, remarks:

"Nernst's formula often leads to absurd ion concentrations—for instance in the case of a copper electrode in a potassium cyanide solution—and it seems unreasonable to assume

$$metal \rightleftharpoons metal\ ion + electron$$
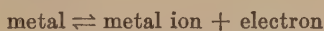
In such circumstances, and in general, the potential between electrode and solution might be defined by means of more direct reactions. For the copper-copper cyanide system we might have:

$$Cu + Cn^- \rightleftharpoons CuCn + \epsilon$$

or $$Cu + 2Cn^- \rightleftharpoons Cu(Cn)_2 + 2\epsilon."$$
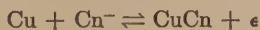
In the case of the oxidation-reduction systems which we have discussed there are cases in which the reductant has high dissociation constants and cases in which it has low dissociation constants. If, in either case, the effectiveness of the reductant were dependent on but one form, *rapidity* in the attainment of electrode potential would not be expected over the entire range of the enormous variation in hydrion concentration used experimentally. Thermodynamics has nothing to say on this matter of rapid attainment of equilibrium. The fact is that no significant variation from a nearly instantaneous adjustment is observed.

In these same cases, analysis suggests that two equivalents are concerned in the oxidation-reduction process. So far as thermodynamics is concerned it is ready to provide equations for the transfer of the equiva-

lents either together or separately and step-wise. Experiment (in the cases under consideration) reveals no trace of step-wise reduction!

Not all oxidation-reduction processes are amenable to study by the electrode method. So far as thermodynamics is concerned it is able to provide a formulation of the free energy of reduction in terms of volt-coulombs or of calories. It is incapable of predicting what systems are and what systems are not amenable to study by the electrode method. The fact that in the cases under consideration there can be generated an electric current and that presumably electrons are sent into the measuring system, must have a significance to mechanism. Cohen, Gibbs and Clark[8] (1924) argued from these *non-thermodynamic aspects* that the essential or determinative factor is the pairing of electrons in the molecule and the impossibility of passing from reductant to oxidant without breaking the original structure with the transfer of an electron pair (in the *specific cases* they discuss).

In emphasizing this aspect they stated that the question of hydrogenation was an incidental matter depending on the hydrion concentration of the solution and the dissociation constant of the reductant. There might have been an inference of a division in time between transfer of electrons and transfer of protons. This and a misunderstanding of the nature of the argument evidently threw Dixon (1927) completely off the theme and led to his placing undue emphasis upon one special formulation the particular nature of which was pointed out in the previous edition of this book and by Clark (1923). The inference of separate steps divided in time is not essential to the conclusion which has to do with the determinative as distinct from the incidental processes convenient to use in formulations.

It will readily be perceived that the non-thermodynamic dimensions of molecular theory have been used in the argument on mechanism. Ionization, pairing of equivalents, an electrical phenomenon, statistical numbers, etc., are the subjects discussed.

The resulting picture is laden with assumptions and some of these are important to the main subject of this book.

The greater part of the troubles mentioned arise from trying to get more out of the mathematical mill than we put into it. When we put into the mill an assumed mechanistic relation (as we eventually must to bring thermodynamics from its ethereal heights to deal with material problems) we shall get out so much of the truth and so much of the limitations as are inherent in the assumption. Since mechanistic concepts are based not on rigid arguments but are attempts to harmonize a picture drawn with imperfect knowledge, there should be on the one hand no hesitancy in artistic efforts toward harmony, and, on the other hand no disposition to impose the artistry where it serves no good purpose.

We suggest the direct action of undissociated molecules in phenomena usually attributed to ions only. It should not be forgotten that this does not place the two kinds of species on a parity. Thermodynamically they

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[8] Clark *et al.*

differ by the energy of formation of the one from the others. There is no inherent reason for undue emphasis upon the transcendent importance of ions as participants in chemical reaction. There is every reason for utilizing the distinction, noted above, in the free energy-changes.

From the foregoing discussions it should be evident that the designation of a particular electrode-solution system depends so far as convenience is concerned upon relations which we seek, it being more convenient in some instances to formulate all data in terms of hydrogen electrode potentials and in other instances in terms of reduction potentials. So far as the actual physical maintenance of electrode conditions is concerned the designation of an electrode as of one or the other type will certainly depend upon a finite ratio of two products, one of which is the reduction product of the other; but the discovery of what these species are is often a most difficult problem for the solution of which the electrode equations by themselves and thermodynamics by itself are not sufficient. Here the methods of general chemistry must be employed. Here also are pitfalls. Nevertheless, in the end, the strength of the accumulating information will doubtless be found to be not in the purely thermodynamic contributions alone nor in the purely statistical contributions alone but in harmonious union.

CHAPTER XIX

The Quinhydrone and Similar Half-Cells

A half-cell which has won favor as a convenient device with which to determine hydrion activity is the so-called quinhydrone electrode. Its development has been due largely to the work of Biilmann and his collaborators. See the résumé by Biilmann (1927).
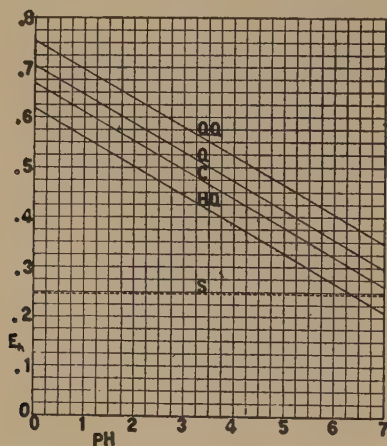
Fig. 78. Relation of Electrode Potential, E_h, to pH

QQ, Quino-quinhydrone electrode; Q, quinhydrone electrode; C, chloranil electrode; HQ, hydro-quinhydrone electrode. Potential of saturated KCl calomel electrode shown by S.

Structurally the half-cell is very simple. An "unattackable" metal, such as gold or platinum, serves as electrode proper. The solution to be examined is saturated with quinhydrone. To complete a cell, the quinhydrone half-cell may be put in liquid junction with a calomel half-cell, with a standard hydrogen half-cell, or with another quinhydrone half-cell in which the solution is a standard buffer.

See page 259 and figure 78 for graphs showing the relation of the potential to pH.

THEORY

Quinhydrone is a peculiar complex formed of equimolecular proportions of quinone and hydroquinone.[1] The first is the "oxidation product" of the second. We shall first regard the quinhydrone as furnishing equimolecular concentrations of an oxidant and reductant.

Whatever may be the actual mechanism by which the one is transformed into the other, we may, for present purposes, assume two, reversible, main steps, of which the second and not the first is, in turn, stepwise.
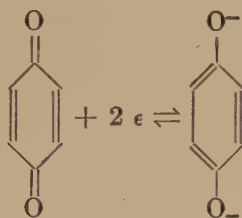
quinone + 2 electrons ⇌ anion of hydroquinone
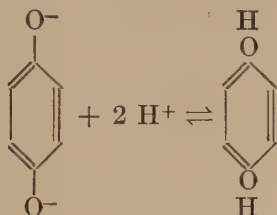
anion of hydroquinone + 2 H+ ⇌ hydroquinone
(stepwise)

The approximate equation for such a system was developed in Chapter XVIII. Its development need not be repeated; but it may be noted that in writing the sum of all forms of reductant and oxidant we should include the dissolved, undissociated quinhydrone, Q. Then the equation is:

$$E_h = E_o - \frac{RT}{2F} \, ln \, \frac{[S_R] - [Q]}{[S_o] - [Q]} + \frac{RT}{2F} \, ln \, [K_1 K_2 + K_1[H^+] + [H^+]^2] \quad (1)$$

[1] Strictly speaking we should speak of benzoquinone and benzohydroquinone, since the terms "quinone" and "hydroquinone" have generic as well as specific meanings.

Here E_h is the observed potential referred to the normal hydrogen electrode, E_o is the characteristic constant of the system, $[S_R]$ and $[S_o]$ are, respectively, the concentrations of *total* reductant and *total* oxidant, $[Q]$ is the concentration of dissolved, undissociated quinhydrone and K_1 and K_2 are the dissociation constants of the reductant. The first dissociation constant of hydroquinone is of the order of 10^{-10} and the second is somewhat lower. Consequently at pH 8 the compound is only about 1 per cent dissociated, at pH 7 about 0.1 per cent dissociated and from then on through the lower values of pH it can be considered *for certain* purposes as completely in the undissociated form. By referring directly to equation (1) we see that, when $[H^+]$ is large (over 10^{-8} for approximate limit) compared to K_1 and K_2 the sum in the last term reduces practically to the value of $[H^+]^2$. Hence, with an approximation that the better approaches the truth the higher the value of $[H^+]$, we may write the last term:

$$\frac{RT}{2F}\, ln\, [H^+]^2 \text{ or } \frac{RT}{F}\, ln\, [H^+].$$

Assuming $[S_R] - [Q] = [S_o]' - [Q]$, we have

$$E_h = E_o + \frac{RT}{F}\, ln\, [H^+] \tag{2}$$

At 25°C., for instance, (2) would be:

$$E_h = E_o - 0.05912\, pH \tag{3}$$

The above was stated in terms of concentrations for the sake of deriving the approximate equation and showing why alkaline solutions should be avoided if (2) is to be applied. The approximation also serves another purpose. It indicates that if we are content to operate in acid solutions we may simplify the development of the more exact equation which is to be in terms of activities.

For the reaction

$$\text{Quinone} + 2\,H^+ + 2\,\epsilon \rightleftharpoons \text{Hydroquinone}$$
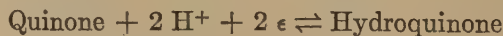
$$\frac{(\text{quinone})\,(H^+)^2\,(\epsilon)^2}{(\text{hydroquinone})} = K$$

Solve for (ϵ) and introduce in equation 15 of Chapter XVIII.

$$E_h = E_o - \frac{RT}{2F} \ln \frac{(\text{hydroquinone})}{(\text{quinone})} + \frac{RT}{F} \ln (H^+) \qquad (4)$$

[Note: In this book *activities* are denoted by () while concentrations are denoted by [].]

For the equilibrium in the reaction

$$\text{quinone} + \text{hydroquinone} \rightleftharpoons \text{quinhydrone}$$

we may write:

$$\frac{(\text{quinone}) \; (\text{hydroquinone})}{(\text{quinhydrone})} = K_q \qquad (5)$$

But, since (quinhydrone) is a constant when the solid phase is present,

$$(\text{quinone}) \; (\text{hydroquinone}) = K_{qs} \qquad (6)$$

Now consider the case when there is added to the quinhydrone in solid phase either quinone or hydroquinone to keep the solution saturated with two of the three substances. Then, in addition to constancy in the activity of quinhydrone which establishes (6), one of the variables in (6) is made constant and hence the other must be.

We need not know the values of (quinone) or (hydroquinone) to know that equation (4) will be reduced to:

$$E_h = E_{qq} + \frac{RT}{F} \ln (H^+) \qquad (7)$$

when *quinone and quinhydrone* are the solid phases. This then is the equation for the system which Biilmann and Lund (1921) call the *quino-quinhydrone electrode*.

Likewise when hydroquinone and quinhydrone are the solid phases equation (4) reduces to:

$$E_h = E_{hq} + \frac{RT}{F} \ln (H^+) \qquad (8)$$

This is the equation for the so-called hydro-quinhydrone electrode.

The values of E_{qq} and E_{hq} may be established independently

by a procedure similar to that noted in determining the characteristic constant of the quinhydrone electrode.

It is to be particularly noted that the only variable remaining at the right of equations (7) and (8) is (H⁺). Therefore, in the sense that nothing that can effect the activities of the quinone, hydroquinone or quinhydrone will affect the potential, these electrodes are said to be "without salt effect." There will be less chance of misunderstanding if we say that, if these electrodes and the hydrogen electrode at constant pressure respond only to changes of (H^+) their potentials should run parallel. Within the limits of experimental error it seems to have been demonstrated that they do.

When quinhydrone is the only component of the solid phase the situation is not so easily simplified. We cannot assume equality of the activities: (hydroquinone) and (quinone); but we may assume equality of the concentrations $[S_o]$ and $[S_r]$, the total oxidant and the total reductant in solution. But, in acid solution,

$$[S_r] - [Q] = [\text{hydroquinone}] = \frac{(\text{hydroquinone})}{\gamma_r}$$

and

$$[S_o] - [Q] = [\text{quinone}] = \frac{(\text{quinone})}{\gamma_o}$$

where [Q] is the concentration of quinhydrone and γ_r and γ_o are the activity coefficients of the hydroquinone and quinone, respectively.

Using the above relations and

$$[S_r] = [S_o]$$

we reach:

$$\frac{(\text{hydroquinone})}{(\text{quinone})} = \frac{\gamma_r}{\gamma_o}$$

Consequently equation (4) becomes:

$$E_h = E_q - \frac{RT}{2F} \ln \frac{\gamma_r}{\gamma_o} + \frac{RT}{F} \ln (H^+) \tag{9}$$

This equation for the true quinhydrone electrode now contains the activity coefficients of the hydroquinone and quinone and,

since the ratio does not remain the same while the constitution of the solution is changed, the electrode exhibits what is called a "salt-effect," which is a special "salt-effect."

Sørensen, Sørensen and Linderstrøm-Lang (1921) confirmed equation (9) by determining γ_r and γ_o through solubility measurements with hydroquinone and quinone. They also traced the details contributing to the conclusions of equations (7) and (8).

Equation (9) in its numerical form for 18°C. may be recast to the form:

$$pH = \frac{E_q - E_h}{0.05773} - 0.5 \log \frac{\gamma_r}{\gamma_o} \tag{10}$$

Linderstrøm-Lang replaces $-0.5 \log \dfrac{\gamma_r}{\gamma_o}$ by Q, the magnitude of

TABLE 54

"Salt correction," Q_s, for quinhydrone electrode at 18°

Add value to $\dfrac{E_q - E_h}{0.05773}$ to obtain corrected value of pH.

SOLUTION	Q_s	SOLUTION	Q_s
0.01 N HCl...............	−0.001	0.5 M $(NH_4)_2SO_4$..........	+0.019
0.02 N HCl...............	−0.002	1.0 M $(NH_4)_2SO_4$..........	0.038
0.05 N HCl...............	−0.003	1.5 M $(NH_4)_2SO_4$..........	0.057
0.10 N HCl...............	−0.005	2.0 M $(NH_4)_2SO_4$..........	0.078
0.01 N HCl + 0.09 N KCl..	−0.009	2.5 M $(NH_4)_2SO_4$..........	0.097
0.04 M NaCl...............	−0.005	3.0 M $(NH_4)_2SO_4$..........	0.116
0.09 M NaCl...............	−0.008	3.5 M $(NH_4)_2SO_4$..........	0.135
0.49 M NaCl....	−0.021	4.0 M $(NH_4)_2SO_4$..........	0.156
0.99 M NaCl...............	−0.045	4.5 M $(NH_4)_2SO_4$..........	0.175
1.99 M NaCl...............	−0.094	5.0 M $(NH_4)_2SO_4$..........	0.194
2.99 M NaCl...............	−0.145		
3.99 M NaCl...............	−0.200		

which must be added to the observed value of $\dfrac{E_q - E_h}{0.05773}$ to obtain the true value of pH. Since this correction term, Q, will vary it is feasible to list only a few cases. Linderstrøm-Lang (1924) gives the values shown in tables 54 and 55. His estimates of the corrections applicable to milk and blood serum are not in very good agreement with those of Lester (1924) on the one hand

or of Kolthoff (1925) on the other hand; but his data are the more carefully rationalized. They may serve to indicate the order of magnitude of the corrections to be expected and for approximate purposes may be considered additive for limited ranges of concentrations. For rough work the salt effect may be ignored as negligible compared with errors of technique.

PREPARATION OF QUINHYDRONE

Biilmann (1927) after some years experience recommends the following method of preparing quinhydrone, the method used by Biilmann and Lund (1921).

TABLE 55

Protein correction Q_p for quinhydrone electrode at 18° at indicated pH value of solution

EGG ALBUMIN	pH	Q_p	SERUM ALBUMIN	pH	Q_p
0.3 Cn*	4.0	+0.003	0.3 Cn*	4.0	+0.048
0.3 Cn	4.5	−0.017	0.3 Cn	4.5	+0.033
0.3 Cn	5.0	−0.028	0.3 Cn	5.0	+0.028
0.3 Cn	5.5	−0.031	0.3 Cn	5.5	+0.029

SERUM ALBUMIN	pH	Q_p	SERUM ALBUMIN	pH	Q_p
0.1 Cn*	4.7	+0.009	0.6 Cn*	4.7	0.045
0.2 Cn	4.7	+0.017	0.8 Cn	4.7	0.055
0.4 Cn	4.7	0.033	1.0 Cn	4.7	0.064

* Cn = gram equivalents of protein nitrogen.

A solution of one hundred grams of iron alum in 300 cc. of water at 65°C. is poured into 100 cc. of a warm solution containing 25 grams commercial hydroquinone. The mixture is cooled, the quinhydrone is filtered with suction and washed three or four times with cold water. Dry between filter paper at room temperature and store in dark bottles. Yield: 15 to 16 grams.

This preparation may contain traces of iron which Biilmann believes to have no appreciable effect on the potential. High temperature drying should be avoided since quinone may volatilize sufficiently to alter the desired ratio of reductant to oxidant.

Schreiner (1925) prefers a purer product. He crystallizes hydroquinone from 50 per cent aqueous acetic acid and quinone from water acidified with acetic acid. For the preparation of quinhydrone from these pure products an acetic acid solution of the hydroquinone is added in excess to an acetic acid solution of the quinone.

Arnd and Siemers (1926) find that occluded acidic impurities may appreciably affect the potential in poorly buffered solutions and therefore they recrystallize the quinhydrone from water at 70°C. Kolthoff (1927) thinks crystallization from water has an unfavorable effect. He extracts the preparation with water before use.

It is not improbable that attempts to prepare quinhydrone of high purity by repeated crystallization have sometimes failed to yield a reliable product because no attention was given to the tendency of the product to oxidize, or otherwise change, in neutral as well as in alkaline solution. While I have had little experience, I would suggest that recrystallization be done in acid solution. As the preparation becomes purer the amount of acid necessary becomes small. Recrystallization in acid solution followed by washing in the absence of air would seem *a priori* to be the better procedure.

ELECTRODES AND ELECTRODE VESSELS

Since the possible effects of atmospheric oxygen in changing the ratio of oxidant to reductant are usually neglected, the common forms of electrode vessel make no allowance for the management of a gas phase as does any well designed vessel for the hydrogen electrode. This simplifies the design. Indeed there is not very much to say about the vessel, unless one describes all the unimportant details which have been made the occasion for papers on the subject.[2]

Biilmann and Lund's vessels are shown by 1 and 2 of figure 79. Biilmann recommends that at least two electrodes be used. Among several vessels designed to handle small quantities of solution may be mentioned that of Cullen and Biilmann (1925), No. 3. The gold plated wire is moistened and dipped into crystals

[2] Apparently we have here a case where multiplicity of design is in direct proportion to the simplicity permissible.
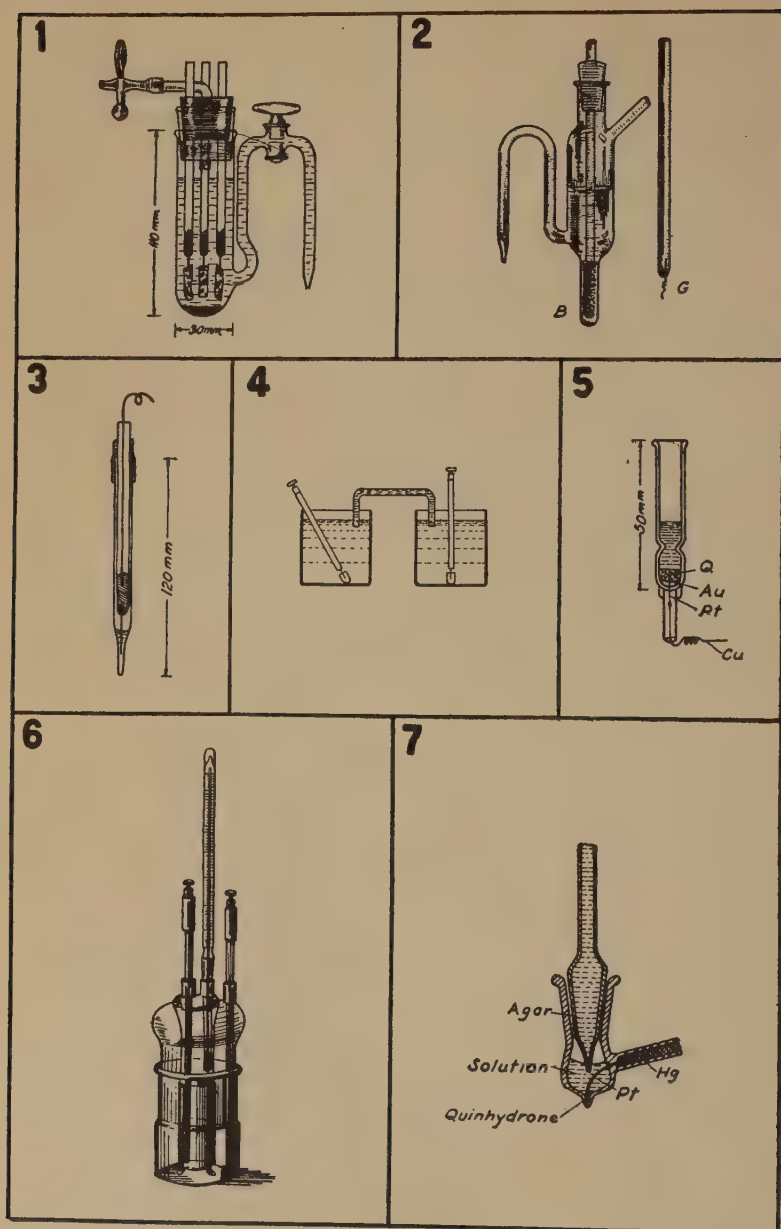
FIG. 79. VESSELS FOR QUINHYDRONE HALF-CELLS

of quinhydrone. These adhere. The electrode is then placed in the capillary and solution is drawn in. The tip of the vessel is then placed in the KCl bridge.

No. 4 is a simple quinhydrone cell, one half-cell of which contains a standard buffer solution, e.g., "standard acetate." The junction is made with a bridge of KCl-agar. This was used by Viebel.

No. 5 represents the vessel of Mozolowski and Parnas (1926). A small platinum wire is fused to a copper lead. The platinum wire runs through the bottom of the vessel and makes contact with a gold film. No. 6 represents one of the vessels of Mislowitzer (1925). One of the compartments carries a reference solution the other the tested solution. Junction is made with KCl solution in the joint. Smolik (1926) uses a similar device.

No. 7 is a micro-electrode vessel designed by Ettisch (1925).

Regarding the electrode itself it may be said that there apply the precautions discussed in Chapter XIV during the description of the preparation of the base of the hydrogen electrode. No "black" is to be deposited but Biilmann emphasizes the necessity for a good and clean surface. There are those who prefer platinum and those who prefer gold surfaces. Biilmann is a bit indefinite regarding his preference; but Corran and Lewis (1924) prefer gold while Mislowitzer (1926) and Grossmann (1927) prefer platinum.

SOURCES OF ERROR

In alkaline solutions two effects must be taken into account. In the first place the ionization of hydroquinone becomes appreciable above about pH 8.5 and renders inapplicable the simplified equation. If the dissociation constants of hydroquinone were accurately known this could be corrected for; but it would not obviate a serious difficulty,—the decomposition and oxidation which takes place readily in the system when subjected to alkaline solutions. See, for example, LaMer and Parsons (1923), LaMer and Rideal (1924), and Conant, Kahn, Fieser and Kurtz (1922). In a more or less arbitrary way Biilmann (1927) sets pH 8.5 as the limit of measurements of the accuracy of 0.01 unit pH but it must be noted that his basis is the effect of dissociation.

A second fundamental consideration is the avoidance of oxidiz-

ing or reducing solutions which can change the ratio of oxidant
to reductant the mainteinance of which is essential. It is by no
means a simple matter to treat this aspect with complete assur-
ance. As indicated on page 371 the complete avoidance of solu-
tions which are potentially capable of exercising a reducing or
oxidizing action would seriously limit the application of any
device for the determination of pH by electrode methods. It
would eliminate the quinhydrone electrode from one of its spheres
of greatest value. For it was shown by Biilmann (1921) in one
of his first papers on the subject that the quinhydrone electrode
may be used to determie the pH values of dilute nitric acid solu-
tions and of solutions of unsaturated organic acids which cannot
be well handled with the aid of the hydrogen electrode. The more
obvious explanation of this success is that the oxidizing or the
reducing agent acts so slowly that the ratio of quinone to hydro-
quinone is not appreciably changed within the time required for
the attainment of the equilibrium in the system quinhydrone-
quinone-hydroquinone-electrode. And here it may be remarked
that the absence of a gas phase, the absence of a complicated
solid phase (platinum black) and the absence of the catalytic
effect of the platinum black probably contribute to the rapidity
of the attainment of equilibrium. Indeed those who are accus-
tomed to the hydrogen electrode and to the necessity of establish-
ing by long waits the fair permanence of potential and the ab-
sence of significant drift of potential will be inclined to use poor
judgment in the application of the quinhydrone electrode. Of
course some time must be allowed for the attainment of equi-
librium. We may reasonably assume that the equilibrum poten-
tial is approached asymptotically; but if we do not seek the utmost
refinement we may rely on the experience (with stable buffer
solutions) that the equilibrium potential is very closely ap-
proached within a very few minutes.[3] Subsequent drifts of
potential in complicated and unstable solutions may then be due
to secondary reactions causing a fundamentally true error in the
measurement. A clear separation of the two effects, asymptotic

[3] The photographic record of potential change made by Buytendijk
and Brinkman (1926) indicates that, in the absence of carbonate, the
equilibrium potential is reached or closely approached within a few seconds
after a change is made in a previously equilibrated system.

approach to equilibrium potential on the one hand and reaction of the oxidation-reduction system internally or with constituents of the solution on the other hand, is probably the greatest puzzle in the practical application of the quinhydrone electrode or of any similar system.

Among the problems which have not yet been adequately solved is that of the conduct of the quinhydrone system in protein solutions. In the first place there occur in the literature scattered references to the combination of quinone with protein. See for example Cooper and Nicholas (1927) and the subject of quinone tanning dealt with in treatises on tanning. Yet the application of the system to the study of milk, beer, blood serum etc. has been fairly successful. A summary with references pertaining to these applications is given in Biilmann's review, (Biilmann, 1927).

True errors caused by reaction of the system with the constituents of the solution must be carefully distinguished from apparent error resulting from the attempt to apply to all sorts of solution the simple equation cast in terms of concentrations or the data standardized with the aid of simplifying assumptions.

There remain a number of sources of error due to faulty technique. Quinhydrone is not always easy to wet. Compare Corran and Lewis (1924). Loss of quinone by drying quinhydrone at too high temperature, the occlusion of oxidation products etc., alter the ratio of oxidant to reductant. In buffer-poor solutions the occlusion of acid or of impurities having a direct effect on the acid-base equilibrium of the solution with which the quinhydrone is mixed have been detected as sources of error. Biilmann (1927) presents an elaborate discussion of the errors of temperature fluctuation. Biilmann cautions against the use of electrodes which have developed minute cracks in the glass seal. It would seem from his discussion that a good part of the false potentials thereby attained is due to the mercury. Let it be noted however that mercury electrodes have been used successfully in similar cases. In the cases cited by Clark and Cohen (1923) the mercury was of very high purity. Compare also Butler, Hugh and Hey (1926).

APPLICATIONS

The quinhydrone and similar self-cells have found many applications. In some instances they have been applied simply as

substitutes for the hydrogen half-cell. However, they have unique uses. The absence of a catalytically active metal and of an intense reducing system has permitted the quinhydrone electrode to be applied to solutions of dilute nitric acid, unsaturated organic acids and a variety of oxidizing systems which either are too slow in their action to appreciably disturb the equilibrium of the electrode or are oxidants of low oxidizing intensity. (See page 391.) Furthermore there is no gas phase and consequently no complexity such as is encountered when the hydrogen half-cell is used with carbonate solutions. This is of particular importance to the study of biological systems.

Because the quinhydrone electrode is much more simple to operate than the hydrogen electrode and yet can be used with the potentiometer system and other equipment provided for the hydrogen electrode, it has been put into practice by very many of those who are already equipped for hydrogen electrode measurements and by those entering the general field for the first time. Because of this it is practically impossible without diligent and detailed examination of the world's literature to assemble a complete list of applications. And yet it is in special applications that there have appeared special sources of error, better knowledge of limitations and the occasions for special technique. These minutiae cannot be covered adequately in a general text. Hence there are assembled below an *incomplete* list of references to applications by subject,—a list which it is hoped will be of use to those who are in search of the records of applicability in their several specialties.

Alkaloids, medicinals, etc.: Baggesgaard-Rasmussen and Shou (1925), Brunius and Karsmark (1927), Wagener and McGill (1925); *Aluminum solutions:* Pelling (1925); *Blood, plasma, serum, etc.:* Corran and Lewis (1924), Cullen and Biilmann (1925), Cullen and Earle (1928), Grossman (1927), Runge and Schmidt (1926), Liu (1927), Meeker and Oser (1926), Mislowitzer (1925, 1926), Schaefer (1926), Schaefer and Schmidt (1925), Vellinger and Roche (1925); *Copper solutions:* O'Sullivan (1925); *Dairy products:* Lester (1924), Knudsen (1925), Linderstrøm-Lang and Kodama (1925), Watson (1927); *Feces:* Robinson (1925); *Gastric juice:* Schaefer and Schmidt (1925), Váná (1926); *Nickel solutions:* Parker and Greer (1926); *Plant-juices:* Dom-

ontvich (1925); *Protein solutions:* Freundlich and Neukircher (1926), Linderstrøm-Lang and Kodama (1925); *Soils:* Arnd and Siemers (1926), Baver (1926), Biilmann (1924), Biilmann and Tovborg-Jensen (1927), Brioux and Pien (1925), Hissink and van der Spek (1926), Itano, Arakawa and Hosoda (1926–1927), Kappen and Beling (1925), Olsen and Linderstrøm-Lang (1927), Schmidt (1925), Snyder (1927); *Sugar solutions;* Balch (1925), Biilmann and Katagiri (1927), Paine and Balch (1927); *Tanning:* Hugonin (1925); *Water (natural):* Parker and Baylis (1926); *Wine:* Dietzel and Rosenbaum (1927); *Titrations, measurements of dissociation constants, theoretical work, non-aqueous solutions, etc.:* Auerbach and Smolczyk (1924), Bodforss (1922), Biilmann and Henriques (1924), Buytendijk, Brinkman and Mook (1927), Conant et al. (1922–1927), Cray and Westrip (1925), Daniel (1927), Darmois (1924), Darmois and Honnelaitre (1924), Ebert (1925), Harris (1923) ,Itano and Hosoda (1926), Klit (1927), Kolthoff (1923, 1927), Kolthoff and Bosch (1927), LaMer and Baker (1922), LaMer and Parsons (1923), LaMer and Rideal (1924), Larsson (1922), Pring (1923, 1924), Rabinowitsch and Kargin (1927), Schreiner (1922, 1925), Sørensen and Linderstrøm-Lang (1924), Wagener and McGill (1925).

THE CHLORANIL ELECTRODE

Among the several quinone-hydroquinone systems studied by Conant and Fieser (1923) and by others, that of tetrachloroquinone and its hydroquinone promises to rival the benzoquinone-benzohydroquinone system in usefulness. With tetrachloroquinone (Chloranil) and the corresponding hydroquinone
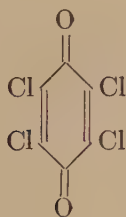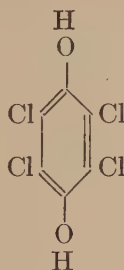
Chloranil   Hydroquinone of chloranil

it is possible to saturate solutions simultaneously with both oxidant and reductant as is not the case with hydroquinone and quinone.

If then a cell be formed as follows

$$\text{Pt} \left| \begin{matrix} \text{C}_6\text{Cl}_4\text{O}_2 \text{ (sat.)} \\ \text{C}_6\text{Cl}_4\text{O}_2\text{H}_2 \text{ (sat.)} \end{matrix} \right| \text{Solution A} \left| \text{Bridge} \right| \begin{matrix} \text{C}_6\text{Cl}_4\text{O}_2 \text{ (sat.)} \\ \text{C}_6\text{Cl}_4\text{O}_2\text{H}_2 \text{ (sat.)} \end{matrix} \right| \text{Solution B} \left| \text{Pt} \right.$$

and if the bridge can be assumed to eliminate junction potential the electrode process is

$$\text{C}_6\text{Cl}_4\text{O}_2 \text{ (solid)} + 2\text{H}^+ + 2\epsilon \rightleftharpoons \text{C}_6\text{Cl}_4\text{O}_2\text{H}_2 \text{ (solid)}$$

Here the end products are solid phases which at a given temperature and crystal form may be regarded as having fixed activities. The free energy change attending the passage of one mole of hydrion from one solution to the other is given at once by **FE** and **E** is the electromotive force of the cell. Obviously the solution must be acid enough to permit the retention of the solid phase of the reductant. The cell potential is then a measure of the relative activities of the hydrion in the two solutions

$$\text{E} = \frac{\text{RT}}{\text{F}} \, ln \, \frac{(\text{H}^+)_A}{(\text{H}^+)_B}$$

Accordingly Conant, Small and Taylor (1925), Hall and Conant (1927) and Conant and Hall (1927) find the chloranil electrode eminently suited to the comparison of solutions with different solvents. See Chapter XXIX.

One difficulty arises in the very small solubility of chloranil and its reductant. Eecause of this the solution rates become important to the approach of an equilibrium potential. Hall and Conant determine by preliminary measurements how much of each substance is necessary to give a quick crystallization when heated to 50° and cooled to the working temperature.

SUMMARY OF EQUATIONS

Quinhydrone electrode

$$\text{E}_h = \text{E}_q + \frac{\text{RT}}{\text{F}} \, ln \, (\text{H}^+) + \text{(a correction term specific for each solution)}$$

For values of the correction term see pages 409–410. Omitting

consideration of the correction term we have the numerical form at 25°C.

$$E_h = E_q - 0.05912 \, pH$$

For the numerical factor at various temperatures see Appendix.

For the cell

$$- \text{Pt, } H_2 \text{ (1 atmos.)} \mid HCl \text{ (0.1N), quinhydrone} \mid \text{Pt} + \qquad \text{I}$$

at 18°C. Biilmann and Jensen (1926) obtain 0.70439 ± 0.00004 volt. Since the difference of potential between the hydrogen and quinhydrone electrodes should be the same at all values of pH in the acid region under ideal conditions, we may regard $+0.7044$ to be the value of E_q at 18°C. Biilmann and Krarup (1924) obtained the following expression for the temperature coefficient of cell (I)

$$E_{ht} = 0.7175 - 0.00074 \, t$$

To conform to Biilman and Jensen's value at 18° we shall use

$$E_{ht} = 0.7177 - 0.00074 \, t$$

Accordingly there can be found the values of E_q given in table 56.

Veibel (1923) recommended the quinhydrone half-cell as one which, if prepared from day to day with a standard solution could serve in the standardization of hydrogen- or calomel half-cells.

When, however, the quinhydrone half-cell is put in junction with saturated KCl solution, as it is in standardizing the saturated calomel half-cell, there is introduced an uncertain liquid junction potential. It then becomes a matter of considerable importance to distinguish the manner in which the two type cells below are to be handled.

$$\text{Hg} \mid \text{HgCl, KCl (sat.)} \mid \begin{array}{c} \text{HCl (0.1N)} \\ \text{quinhydrone} \end{array} \mid \text{Pt} \qquad \text{II}$$

$$\text{Hg} \mid \text{HgCl, KCl (sat.)} \mid \begin{array}{c} \text{Phosphate buffer} \\ \text{quinhydrone} \end{array} \mid \text{Pt} \qquad \text{III}$$
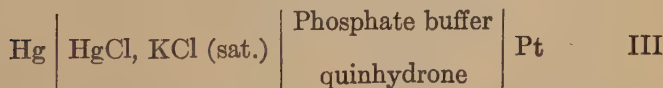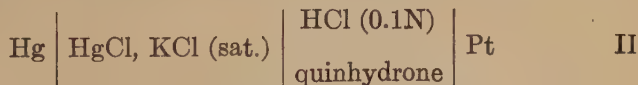
In cell II the liquid junction potential is doubtless much larger than in cell III.

The practice is either to neglect the change or to estimate it by the Bjerrum extrapolation. Partly because of diversity in this practice, and partly because of the discrepancies in primary experimental data involving no calculations, we have been unable reconcile various estimates of numbers used in the practical application of the quinhydrone electrode.

Most of the data assembled by Biilmann (1927) proceed from standardizations with 0.01N HCl + 0.09N KCl but with 2.029 as the assumed pH value.

We shall make the following tentative estimates.

Assume 1.078 for the pH *number* of 0.1N HCl and calculate therefrom the hydrogen potentials at various temperatures. See table A page 672. From these estimates compile with the aid of table A the numbers found in table 56 below.

TABLE 56
Tentative values for cells containing the quinhydrone half-cells

Cell A　　　　　　　Pt, H₂(1 atmos.) | $(H^+) = 1$ / quinhydrone | Pt

Half-Cell B　　　　|| KCl (sat.) | HCl (0.1) / quinhydrone | Pt

Cell C　　Hg | HgCl, KCl (0.1N) | KCl (sat.) | HCl (0.1N) / quinhydrone | Pt

Cell D　　　　Hg | HgCl, KCl (sat.) | HCl (0.1N) / quinhydrone | Pt

TEMPERATURE	CELL OR HALF-CELL			
	A	B	C	D
°C.	volts	volts	volts	volts (approx.)
18	0.7044	0.6423	0.3043	0.391
20	0.7029	0.6404	0.3025	0.390
25	0.6992	0.6356	0.2980	0.3898
30	0.6955	0.6308	0.2937	0.389
35	0.6918	0.6261	0.2896	0.388
38	0.6896	0.6232	0.2871	0.387
40	0.6881	0.6213	0.2855	0.387

See pages 259 and 404 for the position of the line of the quin-hydrone electrode on the E:pH diagram.

Quino-quinhydrone electrode

$$E_h = E_{qq} + \frac{RT}{F} \, ln \, (H^+)$$

or at 25°

$$E_h = E_{qq} - 0.05912 \, pH$$

For the cell

$$- \, Pt, \, H_2(1 \, atmos.) \, \Big| \, HCl \, (0.1N) \, \begin{array}{c} \text{quinone (s)} \\ \text{quinhydrone (s)} \end{array} \, \Big| \, Pt \, +$$
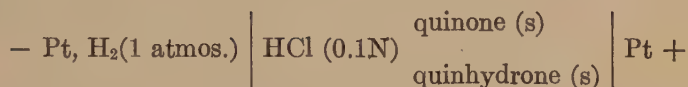
Biilman and Lund (1921) found at 18° 0.7564. Schreiner's (1925) data give

$$E_h = 0.7759 - 0.000842 \, t$$

for the range 5° to 18°. We then have

t	E_{qq}	t	E_{qq}
°C.		°C.	
0	0.7716	18	0.7564
5	0.7674	20	0.7548
10	0.7632	25	0.7505
15	0.7590		

Conant and Fieser (1923) find 0.7488 at 25° and 0.7699 at 0°.

Hydro-quinhydrone electrode

$$E_h = E_{hq} + \frac{RT}{F} \, ln \, (H^+)$$

or at 25°

$$E_h = E_{hq} - 0.05912 \, pH.$$

For the cell

$$- \, Pt, \, H_2(1 \, atmos.) \, \Big| \, HCl \, (0.1N) \, \begin{array}{c} \text{quinhydrone (s)} \\ \text{hydroquinone (s)} \end{array} \, \Big| \, Pt \, +$$
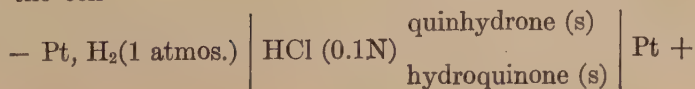
Biilmann and Lund (1921) found at 18° 0.6177. Schreiner (1925) finds a temperature coefficient of -0.000651 volt per degree between 12° and 22° and -0.000641 volt per degree between 22° and 32°. Hence we have:

t	E_{hq}	t	E_{hq}
°C.		°C.	
0	0.6294	20	0.6164
10	0.6242	25	0.6132
15	0.6197	30	0.6100
18	0.6177		

Conant and Fieser (1923) find 0.6126 at 25° and 0.6272 at 0°.

Chloranil electrode

$$E_h = E_c + \frac{RT}{F} \, ln \, (H^+)$$

Conant and Fieser (1923) found that when chloranil and hydro-chloranil are present in the solid phase $E_c = 0.664$ at 25°C. and 0.683 at 0°C.

Note that this not the potential of a homogeneous system (solution) at 50 per cent reduction.

SUMMARY

See Appendix, table A for a table of standardized values.

CHAPTER XX

Metal Oxide Electrodes; The Glass Electrode; The Oxygen Electrode

METAL OXIDE ELECTRODES

Equations

The reversible exchange of electrons between a metal and its ions may be regarded as an oxidation-reduction process. For the system:

$$M^{n+} + n\epsilon \rightleftharpoons M,$$
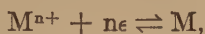
we may write the electrode potential equation (1) directly from equation (15) of Chapter XVIII (page 377).

$$E = E' + \frac{RT}{nF} ln \frac{(M^{n+})}{(M)} \tag{1}$$

Were the metal-metal ion system the only one present, the saturation of the solution with respect to the metal should be accomplished by the presence of a mass of the metal in a solid phase other than that of the electrode itself. **E** should then be determinable by an unattackable electrode. Of course this is quite impracticable because M, specified formally as a component of the solution, has an activity (M) of such an insignificant magnitude that the slightest disturbance of the electrode itself, by the presence of the slightest trace of another oxidation-reduction system, would vitiate the measurement. Consequently in the study of the metal-metal ion system the electrode itself is made of the metal in question in order that this metal may dominate the situation in the immediate interface between electrode and solution.

We develop this point of view in order that we may avoid the confusion arising from the consideration of the electrode as highly specialized. We shall regard it as fundamentally an oxidation-reduction electrode the potential of which may be determined by the system $M^{n+}:M$ or by the system $M^{a+}:M^{b+}$.

In the first case we assume the activity of the metal in solution to be constant and equation (1) reduces to

$$E = E_o + \frac{RT}{nF} \ln (M^{n+}) \qquad (2)$$

Now suppose the alkalinity of the solution is sufficient to form the metal hydroxide. For the reaction

$$M^{n+} + n \ OH^- \rightleftharpoons M \ \underline{OH}_n$$

write the equilibrium equation

$$\frac{(M^{n+}) \ (OH^-)^n}{(M \ \underline{OH}_n)} = K$$

Let the activity of the metal hydroxide in solution be constant by reason of the presence of the solid phase. Then

$$(M^{n+}) \ (OH^-)^n = K_s \qquad (3)$$

Hence by (2) and (3)

$$E = E_o + \frac{RT}{nF} \ln \frac{K_s}{(OH^-)^n} \qquad (4)$$

or

$$E = E_o' + \frac{RT}{F} \ln (H^+) \qquad (5)$$

If, in place of the hydroxide, there is present the oxide it is necessary for purposes of formal treatment to assume that the oxide will attain equilibrium with its hydrated product namely the hydroxide in question, and that this in turn will attain constancy of activity in the solution by reason of the presence of the solid phase. Hence equation (5) should still hold, *if the conditions are met.*

The above theoretical discussion assumed but one oxide. In the presence of two oxides there could be only a pseudo-equilibrium; but that the main result should not be affected were there two oxides in the presence of the metal, is revealed by the following. Consider a metal in two states of oxidation, M^{a+} and M^{b+}.

$$M^{a+} + n\epsilon \rightleftharpoons M^{b+}$$
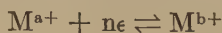
By equation (15) page 377

$$E = E' - \frac{RT}{nF} \, ln \, \frac{(M^{b+})}{(M^{a+})} \tag{6}$$

Using the two solubility products

$$(M^{b+}) = K_b \, (H^+)^b$$

$$(M^{a+}) = K_a \, (H^+)^a$$

we have

$$E = E_o + \frac{RT}{nF} \, ln \, \frac{(H^+)^b}{(H^+)^a} \tag{7}$$

But $b - a = n$. Hence:

$$E = E_o' + \frac{RT}{F} \, ln \, (H^+) \tag{8}$$

Equation (8) is equation (5) again. The reason the same equation is reached may be put in general terms as follows. In addition to those energy changes associated with electron exchange and which are not directly associated with the hydrogen ions or hydroxyl ions, there are involved the energies of ionization of the metal hydroxides and the energy of hydrion dilution. We have assumed that one determinant of the ionization is fixed by the constant activity of the hydroxide or hydroxides. There remains the effect of varying hydroxyl or hydrion concentration. This effect takes the form, in the energy equation, of the free energy of dilution of the hydrions, or hydroxyl ions, according to the choice in formulation. Separating from the free energy change the potential, or intensity factor, we have a relation parallel to the case of the hydrogen electrode. Compare equation (5) or (8) with equation (38) page 390.

The situation would be very different were the hydroxide, or one of two or more hydroxides which might be involved in a pseudo-equilibrium to *not* saturate the solution. Any one of such instances would then become *a very special case* and no common equation would be applicable.

There will be detected in this development several aspects, expressed or implied, which impose difficult experimental restric-

tions. In addition to the difficulty of attaining complete equilibrium with materials so susceptible to acquiring different forms (see for example Maddison, 1926) or degrees of dispersion as are the metal hydroxides and oxides, there is implied the difficulty of controlling the activity of any one form by control of the constitution of the solution. Furthermore it would appear that the water activity must be involved for the ionic product entered the equation in step (4)–(5). This is probably of secondary consequence in most instances.

With the exception of one or two of the simpler cases which have been worked upon, for example the mercury-mercury oxide system, little of a *systematic* nature has been done to illuminate those "oxide electrodes."

THE MERCURY-MERCURIC OXIDE ELECTRODE

Brønsted (1909) finds that the cell

$$- \text{Pt, H}_2 \mid \text{KOH, HgO} \mid \text{Hg} +$$

gives the same electromotive force when the concentration of KOH is changed. There are small differences due to the changing activity of the water. On the assumption of complete dissociation of KOH these findings satisfy equation (5) and the tacit implication spoken of above.

A few references. Brønsted (1909), Donnan and Allmand (1911), Fried (1926), Kolthoff (1916), Lamb and Larson (1920), Chow (1920), Knobel (1923), Fricke and Rohmann (1924), Aten and Van Dalfsen (1926).

THE "ANTIMONY ELECTRODE"

Uhl and Kestranek (1923) used the combination antimony-antimony oxide with promising results. Although they believed that ordinary commercial antimony contains enough oxide to fulfill the requirements, Kolthoff and Hartong (1925) recommend the addition of the oxide. This they prepare by treating antimony with nitric acid, evaporating to dryness and igniting.

In studying the potentials of their electrodes in buffer solutions of known pH-values Kolthoff and Hartong did not obtain the coefficient 0.057 demanded by equation (5) and the temperature

of operation. They found it to be about 0.0485 between pH 1 and pH 5 and approximately 0.0536 above pH 9. Between 5 and 9 their results were erratic.

Buytendijk and Woerdeman (1927) have used this electrode in micro form.

Vlès and Vlès and Vellinger (1927) in a study of the antimony electrode find that the empirical equation

$$pH = 0.0175 \, E + a$$

holds at 24° over a considerable range of pH. In this equation **a** is a constant which must be determined for each particular electrode by measurements with buffer solutions. E is expressed in millivolts. Consequently if E is expressed in volts we have

$$E = 0.05714 \, pH - 0.05714 \, a$$

At 24° the coefficient should be 0.05892.

Dr. Fenwick[1] kindly permits me to quote as follows from the manuscript of a paper entitled *The antimony-antimony trioxide electrode and its use as a measure of acidity* by E. J. Roberts and F. Fenwick. ". . . The potential of the antimony-antimony trioxide electrode attains its maximum accuracy only provided that the presence of any unstable solid phase in the system, notably orthorhombic antimony trioxide, is carefully avoided, dissolved oxygen is eliminated from the solution, and the equilibrium is approached from the alkaline side. Under these conditions the potential of the electrode is a linear function of the logarithm of the activity of hydrogen ion, with the theoretical slope, from pH 1 to 10." Their paper when published should be consulted as the best treatment available. See also Schuhmann (1924).

THE MANGANESE DIOXIDE ELECTRODE

Gesell and Hertzman (1926) prepare the manganese dioxide electrode as follows. A platinum wire about 0.5 mm. diameter is sealed into the end of a glass tube leaving a 1 mm. length protruding. This is rounded with a fine stone "to avoid point effects," plated with platinum black, and fired in an alcohol

[1] Personal communication from Dr. Fenwick.

flame. It is then coated during 1.5 minutes by connecting it to the positive lead of a 6 volt battery while it is immersed in a solution of manganese sulfate ("0.4 N"), acidified with sulfuric acid. The negative electrode was placed 2 cm. from the positive and 650 ohms were placed in the external circuit. According to these authors the above procedure accomplished a compromise between the production of an electrode which adjusts rapidly but which has a coating too thin and too easily dissolved and an electrode which is substantial but sluggish.

That the potential tends to be a linear function of the pH-value of the solution is roughly confirmed; but Gesell, for instance, found with different solutions at pH 7.4 that the potential might vary as much as 0.22 volts corresponding to 3 units pH by the formula deduced above and to 2.3 units pH by Gesell's formula.

Gesell's interest in the manganese dioxide electrode is chiefly as a convenient means of following *changes* for instance in the circulating blood or in the expired air.

Parker (1927) has used the manganese dioxide electrode in control of industrial processes.

References. Tower (1895), Smith (1896), Roaf (1914), Gesell and Hertzman (1926), Gesell and McGinty (1926), Parker (1927).

OTHER OXIDE ELECTRODES

Several other oxide electrodes including those with PbO_2, Ag_2O_3, and Tl_2O_3 were studied by Tower (1895) and occasionally one has been subjected to further study. See for example Kolthoff (1921) and especially Fried (1926). Baylis (1923) found, empirically, promising results with the tungsten filament of an electric light bulb. While the response to pH-changes might be ascribed to a tungsten oxide electrode the relation of pH to potential does not follow that formulated above. Parker and Baylis (1926) made some further studies of its empirical use.

THE OXYGEN ELECTRODE

Theoretically an unattackable electrode under a definite partial pressure of oxygen should give a potential which is a linear function of the pH value of the solution. See equation 22 page 381.

Practically the calculated potential (see figure 77, page 387) is not attained with platinum, gold and other "unattackable" metals, nor is the linear relation always found. Empirically this electrode has been put to use occasionally.

See: Arthur and Keeler (1922), Furman (1922–1923), Goard and Rideal (1924), Malaprade (1926), Montillon and Cassel (1924), Náray-Syabó (1927), Popoff and McHenry (1925), Smith and Giesy (1923), Tilley and Ralston (1923), Van der Meulen and Wilcoxon (1923).

Numerous combinations of electrode metals differing in polarization ability have been put to use in end-point titration. See references in Kolthoff and Furman *Potentiometric Titrations* (1926).

THE "GLASS ELECTRODE"

Imagine a cell of the following type.

Hg | HgCl, KCl (sat.) | solution 1 | solution 2 | KCl (sat.), HgCl | Hg   I
  A   B   C   B′   A′
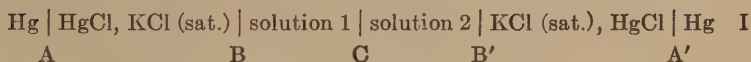
Potentials at A and A′ balance one another. Assume that potentials at B and B′ balance one another. Instead of an ordinary, liquid junction at C imagine some material which permits the passage of a particular kind of ion between solutions 1 and 2. If this ion, i, were alone able to pass, it would tend to go from the solution in which its chemical potential were the higher to the solution in which its chemical potential were the lower and would carry nF per mole. At potentiometric balance the potential of the cell would be

$$\pm \mathbf{E} = \frac{\mathbf{RT}}{\mathbf{F}} \, ln \, \frac{(\mathrm{i})_1}{(\mathrm{i})_2} \tag{10}$$

Suppose solutions 1 and 2 were solutions of silver nitrate with silver ion activities $(Ag^+)_1$ and $(Ag^+)_2$, and suppose the partition at C were metallic silver. Instead of formulating the equation by means of single electrode potentials, we may consider the metallic silver partition to be one permeable only to silver ions. Then by equation (10) we have

$$\mathbf{E} = \frac{\mathbf{RT}}{\mathbf{F}} \, ln \, \frac{(Ag^+)_1}{(Ag^+)_2} \tag{11}$$

Now Haber and Klemenziewicz (1909) found that, with such an arrangement as that stated by schema I, the electromotive force of the cell conformed to the equation

$$E = \frac{RT}{F} \, ln \, \frac{[H^+]_1}{[H^+]_2} \tag{12}$$

when a very thin partition of glass was placed at C.

They regarded the glass as a phase containing water and hydrions and hydroxyl ions at constant concentration. If water penetrates and not the other electrolytes of solution 1 and 2, equation (12) should apply. Michaelis[2] pointed out the analogy between this case and the silver cell mentioned above.

However, Horovitz (1923) showed that equation (12) would express experimental results only under particular conditions and that the nature of the glass and the kind of ions in solution are of great importance. Accordingly he formulated in terms of ionic exchange between glass and solution, thereby taking into consideration the specific properties of the glass. Another method of approach is suggested by Michaelis' study of membrane permeabilities. See Michaelis (1926). Should it happen that the ionic mobility of the hydrion in a particular membrane is much larger than that of any other ion there would be a virtual *approach to* the condition leading to equation (12).

See Hurd, Engel and Vernon (1927) on ion replacement in glass.

Horovitz presented a paper on the theoretical aspects at the Richmond Meeting of the American Chemical Society in April, 1927, but I have not noted its publication.

In all events the matter reduces very largely to a selection of glass which will give the desired effect. Considerable information on this aspect was furnished by Horovitz (1923), Horovitz, Horn, Zimmermann and Schneider (1925) and Horovitz and Zimmermann (1925) who showed that certain glasses could function apparently as "sodium electrodes," "potassium electrodes," "zinc electrodes," "silver electrodes," etc., according to their composition and the solutions in contact. In a solution containing sodium ions the well known thermometer glass 59 III and glass 397 III (a soda glass) behaved as "sodium electrodes." Geräte-

[2] See Perlzweig's translation (1926).

glas 16 III and glass 1447 III, which contain zinc, behaved as "zinc electrodes." A number of glasses were also found to function as "silver electrodes" in solutions of silver nitrate. Miscellaneous lead glasses functioned fairly well as "hydrogen electrodes."

For the purposes of ordinary measurements with buffer solutions it is difficult to judge the conduct of particular glasses from Horovitz's papers. He employed none of the common buffer solutions and the hydrogen electrode function was judged by acid-alkali cells.

Kerridge (1925) obtained poor results with "Durosil" glass and fused silica and reported glasses which acted as mixed "sodium-" and "hydrogen electrodes" in sodium phosphate buffers and as "hydrogen electrodes" in potassium phosphate buffers. Among the glasses acting as mixed electrodes were borosilicate glasses. She reports success with "an ordinary soft soda laboratory glass."

Hughes (1928) concludes that a glass should be as free as possible from potash, alumina and borates. He suggests a glass made of 72 per cent SiO_2, 8 per cent CaO and 20 per cent Na_2O. The bulb should be blown as rapidly as possible to avoid devitrification.

APPARATUS

Wolf (1927) gives references to some earlier uses of glass membranes.

Helmholtz (1881) in his picture of what was one of the first "glass electrodes," used a bulb as did Haber and Klemensiewicz. Others have continued the use of a bulb of extremely thin glass blown from the end of a piece of relatively thick glass tube. Kerridge (1925) introduced more convenient and more rugged designs one of which is shown in figure 80. The chief feature is to give to the glass membrane the form of a deep spoon which is "0.025 to 0.030 mm. thick in its thinnest part." This is filled with the unknown. On the other side of the membrane is placed a buffer solution of known pH-value.

Kerridge states that newly blown vessels require careful cleaning with hydrochloric acid, steaming for two hours and soaking

with distilled water for 24 hours before use.   The cell used is according to the following scheme.

Hg | HgCl, KCl (sat.) | Solution 1 | ⌡ | Solution 2 | KCl (sat.), HgCl | Hg
glass
membrane
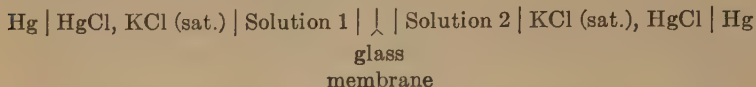
In the figure the vessel is shown mounted with two calomel half-cells.
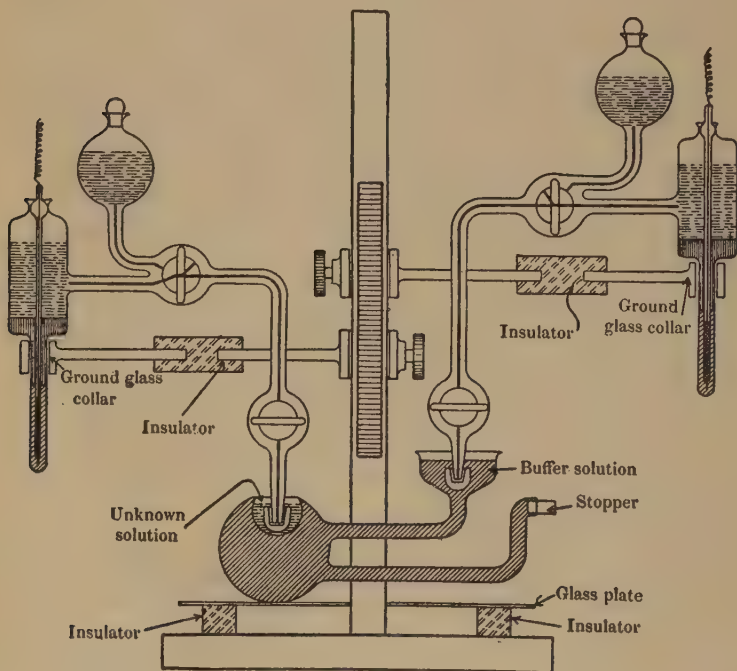
FIG. 80. THE CELL

Hg | HgCl, KCl (sat.) | Unknown | Glass | Buffer | KCl (sat.), HgCl | Hg
Kerridge's Mounting of "Glass Electrode," showing spoon form.

The "insulator" indicated in the figure is "amberite" or "orca." Blocks of such material support the calomel half-cells from the stand through rack-and-pinion adjustors.   For further details of insulation, etc., see Brown (1924) and for description of quadrant electrometer see page 338.

"Diffusion of potassium chloride into the solution in the glass

electrode is prevented by small ground caps fitted over the tips of the calomel electrodes and the two taps, ungreased in the middle race, are turned off while the measurements are being made." The caps are rinsed and wiped before immersion.

If, for instance, acid potassium phthalate is used as the buffer within the vessel and its pH value be regarded as 3.97, the formula should be according the Kerridge (1926):

$$pH = 3.97 \pm \frac{E_s - E_x}{0.0577} \text{ at } 18°C.$$

where E_s is the potential found with the phthalate and E_x is that found with the solution under test.

Kerridge (1926) claims an accuracy characterized by a probable error of 0.01 pH unit. This requires of the quadrant electrometer alone a sensitivity capable of detecting ± 0.6 millivolt.

Reliability of results are suggested by the following comparisons:

Blood by glass electrode method............................ 7.75
Blood by Dale-Evans method............................... 7.73
Phosphate solution by glass electrode method.............. 7.37
Phosphate solution by H-electrode method................. 7.39
Sycamore leaves, extract, by glass electrode method........ 4.88
Sycamore leaves, extract, by H-electrode method........... 4.91

For further details of theory and practice see: Bayliss, Kerridge and Verney (1926), Borelius (1914), Brown (1924), Cremer (1906), Freundlich (1921), Freundlich and Ettisch (1925), Freundlich and Rona (1920), Gross and Halpern (1925), Haber and Klemensiewicz (1909), Hoet and Marks (1926), Hoet and Kerridge (1926), Horovitz (1923) (1925), Horovitz and Zimmerman (1925), Horovitz, Horn, Zimmerman and Schneider (1925), Hughes (1926-1928), Katz, Kerridge and Long (1925), Kerridge (1925), Kerridge (1926), Schiller (1924), and v. Steiger (1924).

The way to be safe is never to feel secure.—BURKE.

ERRORS OF TECHNIQUE

Sources of error are legion. Some of them are specific to the hydrogen electrode; some of them are specific to the quinhydrone electrode; some of them may arise in the use of any cell; occasionally one evinces the stupidity of the operator.

During a series of measurements it became necessary to empty and refill a horizontal tube having a stopcock. Potentials became erratic. This was traced to a bubble of gas which had clung to the bore of the stopcock key. To avoid this the "horizontal" had been given a pitch but the flow had not been adequate that time. One day after a year or so of smooth operation potentials became erratic. The drain tube from the electrode vessel emptied through a six inch air gap to the laboratory drain. The tube was hidden for aesthetic reasons, and it had not been observed that a stalagmite and a stalactite of KCl were forming. On the day in question they met! Not only was faith in the shielding shattered and the shielding redone; but the hiding of the drain tube and even remote connection with the piping became taboo.

These little incidents from the writer's experience are cited merely to suggest the constant watchfulness both in the design of apparatus and in its operation which is necessary. How often has it been suggested that the high tension charging line and the delivery line of the potentiometer's storage battery be placed on a double throw, double pole switch! This neat scheme pleases till some damp day at the end of which a day is counted lost.

The reader, if he counts himself an experimenter, knows full well the impossibility of attempting to caution on every point of technique. Something must be left to common sense and if this is not possessed, how hopeless is the task of going over *in absentia*

the details of a measurement in an attempt to trace a suspected
fault. The hoarding of solutions which should be used to wash
away the buffer action of solutions previously occupying the
electrode vessel, miserly supplies of hydrogen, contamination of
standard half-cells by the solutions of liquid junctions, electric
leakage, poor reproduction of liquid junctions, dirty electrodes,
forgetfulness of hysteresis in cells subjected to temperature
changes, neglect of corrections for particular half-cells, barometer
changes etc., plain carelessness and ordinary stupidity all usually
disappear at the hands of anyone who understands the ele-
mentary theory of his device and sets about it to meet the require-
ments of that theory. Then day after day as the eye is taken
from the galvanometer at balance the readings of the poten-
tiometer dial are found to hit the mark within ± 0.1 millivolt for
the same solution and confidence that something definite is being
measured becomes conviction. And at last, when cells and condi-
tions are changed and small, distinct discrepancies appear, the
experimenter learns to his sorrow that he has yet to master many
a detail of technique.

ERRORS ARISING FROM THE INHERENT LIMITATIONS OF THE HYDROGEN ELECTRODE

Presence of oxidizable material

We have already discussed in Chapter XVIII the relation be-
tween the hydrogen electrode and the "reduction electrode," and
have shown that no true hydrogen electrode potential can be
attained until the solution is so far reduced that it can support one
atmosphere of hydrogen. It is thus made perfectly obvious that
a measurement of pH must be preceded by a very thorough reduc-
tion of the solution.[1]

The hydrogen electrode if properly treated gives such a pre-
cisely defined potential in well buffered solution, reaches this
potential so rapidly, returns when polarized, and adjusts itself to
temperature and pressure changes so well that there is little doubt

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[1] In some instances it is important to remember that reduction of the
constituents of a solution may so change the acidic or basic properties of
these constituents that serious shifts in pH may occur.

of its being a reversible, accommodating, fairly quick-acting electrode. It is perhaps because of this that it shows a hydrogen electrode potential in solutions which could be slowly reduced by hydrogen. For instance there are many organic and inorganic substances which theoretically may be reduced by any system having the reduction potential of the hydrogen electrode, but which, nevertheless, give stable and reproducible potentials as of the acid-base equilibria of their solutions and without being appreciably reduced. It is simply that advantage is taken of the rapidity in the adjustment of the acid-base equilibria and the comparatively great slowness in the adjustment of the oxidation-reduction equilibria. One is almost afraid to estimate the limitations which would be placed upon the hydrogen electrode were this not so. Not only would there be left hardly a biological solution suitable for the measurement but many an inorganic solution which the physical chemist has studied with the utmost care and with supreme confidence in the measurements would be thrown out of court.

In a sense we face a paradox. We prepare the electrode to catalyze reduction and yet must avoid that "thorough" reduction which almost inadvertently was specified in one of the paragraphs above.

It is impracticable to list all the systems which are incompatible with a hydrogen electrode potential. The practical way to deal with the problem is to assume that a rapid attainment of electrode equilibrium and its maintenance after attainment is evidence that the small amounts of oxidants such as oxygen, ferric iron etc. which are frequently present, have been reduced and that no important constituent of the solution is "depolarizing" the electrode.

Evans (1921) has maintained that in the electrometric measurement of carbonate solutions the carbonate is reduced to formate and that for this reason previous measurements of the pH of blood have been in error. There are various reasons for doubting the validity of Evans' last conclusion; but, since the question is one of fact, Cullen and Hastings (1922) have investigated the matter and have failed to confirm Evans. Martin and Lepper (1926) concur with others in believing that Evans criticism has

little significance in measurements of bicarbonate solutions of ordinary strength but they believe they have detected the formation of formic acid in solutions of bicarbonate so dilute (0.0002 M) that the minute amount of the stronger acid formed makes an appreciable difference in pH. Since these investigators employed phenol red and neutral red to show the pH-change and did not recognize, or at least did not discuss, the changes which may take place in these indicators on reduction, their observations must be repeated and their conclusion regarded with caution. See also comments on Evans' objection by Conway-Verney and Bayliss (1923).

Oakes and Salisbury (1922) threw doubt on the reliability of the phthalate solution which Clark and Lubs (1916) recommended as a convenient working standard for checking hydrogen electrode measurements. Clark (1922) repeated some experiments which might have revealed the instability of the phthalate solution at the hydrogen electrode but found no sign of electrode drift. See also Wood and Murdick (1922). Draves and Tartar (1925) believed they had shown the nature of the discrepancy when they found that, under ordinary conditions, the phthalate solution is stable but that with heavy coatings of platinum black appreciable *reduction* of phthalate occurs. Yet Blackadder (1925) refers to his preference for very heavy coatings of platinum black on his electrodes and at another part of his paper remarks that his measurements "have invariably checked with the published pH figures of an M/20 potassium acid phthalate solution, namely 3.97" (Clark and Lubs' value). Evidently the last word on this subject has not been said. However, Clark and his co-workers continue to use phthalate as a working standard, having never observed discrepancies with highly purified preparations.

The depolarizing action of such solutions as those of ferric iron is rapid. However, it is interesting to note that the hydrogen-hydrogen ion equilibrium also adjusts rapidly, and that, if it be given its opportunity, it can compete fairly well. I once had occasion to attempt the measurement of the pH value of a ferric chlorid solution with the hydrogen electrode! A reasonable magnitude was obtained by use of initial potentials as the electrode in a shaking vessel descended into the solution. Of course

the values were quite unreliable and are not to be compared with initial potentials taken with the much more rapidly adjusting oxidation-reduction electrode such as the quinhydrone electrode. I would never have had the courage to mention these very crude experiments had Browne (1923) not had reasonable success with ferric oxide hydrosols containing *small* quantities of ferric chloride. He presaturates the electrode with hydrogen and thrusts it into the liquid, taking the first potentiometric reading, which he says remained fairly constant for a few seconds. He used three or four electrodes to fix the approximate value for the setting of the potentiometer and then operated with several other electrodes.

The effect of an intense and active oxidizing agent will be at once recognized. At the other extreme are the cases where no drift of the E.M.F. in the direction of an oxidizing action at the hydrogen electrode will be detected. Between these extremes lie the subtle uncertainties which make it advisable to check electrometric measurements with indicator measurements and to apply tests of reproducibility, of the effect of polarization, of the effect of time on drift of potential and all other means available to establish the reliability of an electrometric measurement in every doubtful case.

POISONS

There are effects of unknown cause which are included under the term "poisoned electrodes." An electrode may be "poisoned" by a well defined cause such as one of those to be mentioned presently; but occasionally an electrode will begin to fail for reasons which cannot be traced. There is hardly any way of putting an observer on his guard against this except to call his attention to the fact that if he is familiar with his galvanometer he will notice a peculiar drift when balancing E.M.F.'s.

Adsorption of material by the platinum black (with such avidity sometimes that redeposition of the black is necessary), the deposit of films of protein, have been detected as definite causes of electrode "poisoning." Kubelka and Wagner (1926) call attention to the coating of the electrode by deposits of colloidal material in the solutions they studied. For rough measurements they believe it permissible to avoid the effects of such coatings by pushing the wire of the Hildebrand type electrode deeper into the

solution to expose new surface.   In measuring a series of protein solutions or other solutions from which gummy precipitates may form, it is good practice to make the measurements in the order of increasing solubility. This will tend to protect the electrode from becoming clogged.

Michaelis (1914) places free ammonia and hydrogen sulfid among the poisons.   However, there is no special difficulty in obtaining hydrogen electrode potentials agreeing with colorimetric measurements in bacterial cultures containing distinct traces of ammonia or hydrogen sulfid. My recollection is that Sørensen has not expressed worry over the reliability of measurements with protein solutions containing ammonium salts.   (See, for instance, Sørensen, Linderstrøm-Lang and Lund (1926).)   Aten and Van Ginneken (1925) record consistent values for the basic dissociation constant of ammonia as measured with solutions 0.2 M with respect to ammonia in ammonium chloride solutions.   Yet Prideaux and Gilbert (1927) quote Bottger as saying that the hydrogen electrode is untrustworthy with ammonia and some amines.

Alkaloids have been listed as electrode "poisons."   (Isgarischev and Koldaewa (1924).)   Yet alkaloids have been titrated frequently with the hydrogen electrode as end point indicator and their dissociation constants have been measured by hydrogen electrode equilibrium studies by Prideaux and Gilbert (1927).

Britton (1925) finds the electrode to function poorly in the presence of sulfur and sulphites.

The mercury ions which may diffuse into the hydrogen electrode vessel from the calomel electrode have been the cause of a caution by Harned (1926) and by Bovie and Hughes (1923).   The latter used a rather drastic means of prevention.   They introduced a very thin *glass* partition between the calomel electrode vessel and the bridge of pure KCl solution.   They could still get current enough for they used the quadrant electrometer as null-point instrument.   With proper design of the flushing arrangements, this drastic precaution seems quite unnecessary.

Koehler (1920) uses several cocks and flushing side-tubes for protection.

Aten, Bruin and Lange (1927) have studied the poisoning action of As_2O_3.   They distinguish two phases, acute and permanent,

and say that although there may be complete or partial recovery from the first the permanent effect may increase. They also say that $HgCl_2$ behaves like As_2O_3, that H_2S and KCN have but slight poisoning effects and that the hydrolysis of KCN in solution may be studied with the hydrogen electrode.

Of the antiseptics used in biological solutions Michaelis (1914) states that neither chloroform nor toluol interfere if dissolved. Chloroform may hydrolyze to hydrochloric acid. Drops of toluol, however, affect the electrode. Phenol is permissible but of course in alkaline solutions participates in the acid-base equilibria. While he gives no details Schmidt (1916) apparently finds the presence of octyl alcohol permissible. This he uses to prevent frothing of protein solutions. Without study of details I have used octyl alcohol for the same purpose and find no reason to doubt Schmidt's conclusion.

There is an extensive literature upon the so-called "poisons" which interfere with the catalytic activity of the finely divided noble metals used on the hydrogen electrode. This literature is most suggestive, but there is still need for more direct studies of the conditions surrounding the catalytic activity of the hydrogen electrode.

Simply for the sake of clearness we may distinguish two functions of the electrode. The electrode is first of all a convenient third body by which there is established electrical connection with the system, hydrogen-hydrogen ions. That the equilibrium of this system should not be disturbed by the presence of a substance "poisoning" the catalytic activity of the platinum black has been tacitly assumed in the derivation of the thermodynamic equation for electrode potentials. If the reduction of the solution could be accomplished without dependence upon the catalytic activity of the electrode, it should be theoretically possible to attain a true hydrogen electrode potential even in the presence of a substance acting as a poison of catalysis.

Aten, Bruin and Lange (1927) say: "In order to test whether a hydrogen electrode is poisoned, a small quantity of oxygen, for example 0.05 per cent, may be added to the hydrogen and the effect of stopping the hydrogen current may be observed. If there is no rise of potential in the first case, and no decrease in the second, one can be fairly sure that there is no poisoning effect.

If there is a poisoning substance present, the best way of working is to use an electrode of large area, covered with finely divided platinum black, to have the hydrogen as free of oxygen as possible and to stop the hydrogen current before taking a reading."

Hammett (1923) has made an interesting study of the potentials of hydrogen electrodes when oxygen in definite proportions is added to the hydrogen. He finds that the change of potential for any given percentage of oxygen varies with the condition of the platinum, a fact which may be attributed to variation of the catalytic activity. On long exposure to hydrogen the electrode becomes so sensitive to oxygen "that no reasonable precautions can give correct results." For instance in a phosphate buffer after an hour or so the addition of 0.009 per cent O_2 gave only 0.02 millivolt change and 0.43 per cent O_2 4.0 millivolts change. But twenty hours later 0.048 per cent O_2 caused 8 millivolts change. The sensitiveness becomes greater in alkaline solution. Thus the addition of 0.046 per cent O_2 to the hydrogen gave:

with 0.1 M HCl	0.00 mv. change
with phosphate buffer	0.38 mv. change
with 0.1 N KOH	20.00 mv. change

This is doubtless one of the chief reasons for the difficulty in making precise measurements of alkaline solutions.

It is, therefore, appropriate to note the following *relative* rates of diffusion of gases through rubber

GAS	RATE
Nitrogen	1.00
Air	1.15
Oxygen	2.56
Hydrogen	5.50
Carbon dioxide	13.57

In refined measurements the use of rubber tubing is avoided whenever possible. Regarding the effects of oxygen which diffuses through rubber see Biilmann and Jensen (1927). With an electrode in 0.1 N HCl 50 cm. of rubber tubing made a difference of 0.13 millivolt. But see above for alkaline solutions.

That the catalytic action of the "black" need not be present

at the electrode itself has been shown by Bjilmann and Klit (1927). They obtain good hydrogen potentials with blank platinum when colloidial palladium is used *in the solution*.

In ordinary practice an electrode is used not only as an electrode *per se* but also as a hydrogenation catalyst. As such it is very sensitive to "poisons." "Poisons" are then to be regarded as the cause of sluggish electrodes. Among these we find all degrees. Hydrogenation to a point compatible with a true hydrogen electrode potential may be delayed but slightly and we may say that the electrode is a bit slow in attaining a stable potential without our ever suspecting a "poison," or the "black" may be so seriously injured that it becomes entirely impractical to await equilibrium.

And just as "poisons" may render an electrode useless for practical measurements, so the employment of accelerators of catalysis may promote efficiency. With the exception of a brief, unpublished note by Bovie little work has been done in this direction.

The attempt by Centnerszwer and Straumanis (1925) to affect the potential of a hydrogen electrode by radium emanation gave negative results.

UNBUFFERED SOLUTIONS

Not infrequently the attempt is made to measure potentiometrically the pH value of an unbuffered solution such as that of KCl. It is not entirely the fault of the method but rather of the nature of the solution that this is a task requiring the very highest refinements known to experimental art. If for the sake of the argument we assume that the solution under examination is that of a *perfectly* neutral salt having under *ideal* conditions a hydrogen ion concentration of 0.000,000,1 N, a simple calculation will show what an enormous displacement in pH will be caused by the admittance of the slightest trace of CO_2 from the atmosphere, of alkali from a glass container, of impurities occluded in the electrode or of impurities carried into the solution with the solvent or solute. Conversely, even if the measurement were such as to give the true value under ideal conditions it would have little practical significance because of the difficulty in holding the conditions ideal.

By the same reasoning it appears probable that it would be

difficult to obtain true electrode potentials even with a potentiometric system drawing no current during its adjustment. When no buffer is present there is a negligible reserve of hydrogen ions. But the introduction of the electrode with its enormous surface must displace the equilibrium. How much the displacement will be depends both on relative proportions of electrode and solution and on the technique used.

The writer can see little practical use in attempting electrode measurements with unbuffered solutions and would prefer indirection in the treatment of certain theoretical matters which might be illuminated were reliable measurements available.

There are however instances in which it is very desirable to obtain measurements of *slightly* buffered solutions. Various extracts and washings reveal the condition of their source if carefully measured. If the retention of the acid of the electrolyzing bath by the black of the electrode can be avoided and if the absorptive nature of the black can be reduced, there seems to be inherent in the electrode method greater delicacy than in the use of very dilute indicator solutions which are often the preferred means of studying slightly buffered solutions. Beans and Hammett (1925) seem to have accomplished this by preparing catalytically active, *smooth* deposits of platinum. They obtain such deposits by using *pure* chloroplatinic acid.

PARTICIPATION OF CO_2

From what has already been said, the effect of the presence of oxygen is obvious. Indifferent gases such as nitrogen may be considered merely as diluents of the hydrogen and as such must be taken into consideration in accurate estimations of the partial pressure of hydrogen. Gases like carbon dioxid on the other hand act not only as diluents but also become components of any acid-base equilibrium established in their presence.

In very many instances biological fluids contain carbonate and the double effect of the carbon dioxid upon the partial pressure of the hydrogen and upon the hydrogen ion equilibria render accurate measurements difficult unless both effects are taken into consideration and put under control.

At high acidities in the neighborhood of pH 5 carbon dioxide will have *relatively* little effect upon a solution buffered by other

than carbonates.[2]   As the pH of solutions increases, the participation of CO_2 in the acid-base equilibria becomes of more and more importance.   The CO_2 partial pressure in equilibrium with the carbonates of a solution is a function of both the pH and the total carbonate.   If, however, we consider for the sake of the argument that the total carbonate remains fairly low and constant, the CO_2 partial pressure becomes less with increase in pH while its effect upon the hydrogen ion equilibria increases with increase in pH.   Therefore it may be said that it is of more importance under ordinary conditions to maintain the original CO_2 content of the solution than it is to be concerned about the effect of CO_2 upon the partial pressure of the hydrogen.   Furthermore the effect of diminishing the partial pressure of the hydrogen is of *relatively* small importance.

For these reasons the bubbling of hydrogen through the solution is to be avoided unless one cares to determine the partial pressure of CO_2 which must be introduced into the hydrogen to maintain the carbonate equilibria and then provides the proper mixture (Höber 1903).   Cf. Schaede, Neukirch and Halpert (1921). The method usually employed is to use a vessel such as that of Hasselbalch, of McClendon or of Clark in which a preliminary sample of the solution can be shaken to provide the solution's own partial pressure of CO_2, and in which there is provision for the introduction of a fresh sample with its full CO_2 pressure. The hydrogen *supply* is then kept at atmospheric pressure and the *partial* pressure of hydrogen *in* the electrode vessel is either considered to be unaffected by the CO_2 pressure or corrected from the known CO_2 pressure of the solution under examination.

Another method is to employ such a ratio of solution volume to gas volume that the loss of CO_2 from the solution into the gas space is insignificant.   [Compare Michaelis (1914), Swyngedauw (1927), Etienne, Verain and Bourgeaud (1925).]

Of course, in cases where the total carbonate in solution rises to considerable concentrations, the partial CO_2 pressure may become

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[2] Like so many problems of this kind it can be adequately solved only by use of quantitative data.   No *definite* limit, such as pH = 5, can be given.   The relative effectiveness of a given partial pressure of CO_2 depends upon the total carbonate and the pH region.   See page 561.   By "carbonate" is meant either carbonate or bicarbonate.

of very significant magnitude and its effect in lowering the hydrogen pressure must be carefully considered.

With the demand for ever higher accuracy in the study of solutions containing carbonates a return is being made to Höber's (1903) practice of supplying in the hydrogen stream or atmosphere the desired partial pressure of CO_2. See for instance Warburg (1922) and Walker, Bray and Johnston (1927).

CRITERIA OF RELIABILITY

The criteria of reliability of hydrogen electrode measurements are difficult to place upon a rigid basis but certain practical tests are easy to apply. Reproducibility of an E. M. F. with different electrodes and different vessels is the foremost test of reliability, but not a final test. Second is the stability of this E. M. F. when attained. In case flowing hydrogen is used the potential should be the same with different rates of flow. It is not always practicable to distinguish between a drift due to alteration in the difference of potential at liquid junctions and a drift at the electrode but in most cases the drift at the liquid junction is less rapid and less extensive than a drift at the electrode when the latter is due to a failure to establish a true hydrogen-hydrogen ion equilibrium. A test which is sometimes applied is to polarize the hydrogen electrode slightly and then see if the original E. M. F. is reëstablished. This may be done sufficiently well by displacing the E. M. F. balance in the potentiometer system. Where salt and protein errors do not interfere, the gross reliability of a hydrogen electrode measurement may be tested colorimetrically. This checking of one system with the other is of inestimable value in some instances as it has proved to be in the study of soil extracts. There the possibilities of various factors interfering with any accurate measurement of hydrogen ion concentration dimmed the courage of investigators until Gillespie (1916) demonstrated substantial agreement between the two methods. Subsequent correlation of various phenomena with soil acidity so determined has now established the usefulness of the methods.

In addition to the tests so far mentioned there remains the test of orderly series. Certain of the general relations of electrolytes are so well established that, if a solution be titrated with acid or alkali and the resulting pH values measured, it will be known

from the position and the shape of the "titration curve" whether the pH measurements are reasonable or not. This of course is a poor satisfaction if there is any reason to doubt the measurements in the first place but it is a procedure not to be scorned.

TEMPERATURE VARIATIONS

The effect of temperature variations upon the accuracy of electrometric measurements is a question upon which it is difficult to pass judgment. Of course, if measurements are not intended to be refined, one may assume the temperature of the room to be the temperature of the system at the moment of the electrical measurement. It is then a simple matter to select from tables the values and factors applicable at the selected temperature. Since such a procedure introduces errors which are not serious for many purposes, insistence upon temperature regulation may be open to criticism as an unnecessary luxury. Those who take this position are doubtless able to escape the psychological effects of uncertainty, but they can hardly escape the inconvenience of having to deal with new values and new factors with every shift in temperature. Temperature control so simplifies rough measurements that much time is saved, and for this reason is recommended even when it is unnecessary. But before the practice of neglecting temperature control can have scientific standing it needs more experimental investigation than it has been accorded. Calculations are quite insufficient for we have little data upon the hysteresis in the adaptation of different systems to temperature variation. Thus Hammett (1922) notes that although the cell

$$Hg \mid HgCl, KCl \text{ (sat.)} \mid HCl \text{ (0.1 M)} \mid Pt, H_2$$
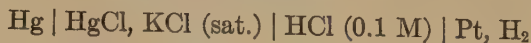
has a comparatively small temperature coefficient, it is very sensitive to sudden changes of temperature.

Cullen (1922), finding that the temperature in an electrode vessel is seldom that of the surrounding air in a room subject to temperature variation, has devised a modification of the Clark electrode vessel whereby the temperature of the *solution* can be measured. The same modification can easily be made in a calomel electrode vessel.

Of course no data for which accuracy is claimed should ever be

reported without there having been temperature control of appropriate accuracy. In view of the hysteresis that may occur a mere record of the temperature at a given moment is of no use, nor is it worth while to attempt calculations of "temperature corrections."

ERRORS WITH THE QUINHYDRONE ELECTRODE

See Chapter XIX, page 414.

CHAPTER XXII

TEMPERATURE COEFFICIENTS

An isolated system obviously cannot be said to have reached equilibrium until the temperature is the same in all its parts.—EASTMAN.

In deriving the type equation

$$\frac{(H^+)\,(\bar{A})}{(HA)} = K_a$$

we assumed constancy of temperature as one of the fundamental conditions. If this equation can be satisfied at one fixed temperature, it is to be presumed that it can be satisfied at another fixed temperature; but it is also to be presumed that each change in the temperature to some new value will result in a new value for K_a. Therefore it would be necessary to determine the values of K_a for a series of fixed temperatures if the temperature coefficient of K_a is to be determined. At each temperature the value of K_a would be determined by the specific properties of the components of the system at that temperature and the temperature coefficients of K_a would not be predicted from any universal rule of conduct with an accuracy sufficient for our purposes.

The same would be true of the activities of the hydrions in a solution of some specific, completely ionized acid.

Most of the data of our subject rest ultimately upon measurements of hydrogen cells. In the treatment of these cells it is agreed that the standard of reference shall be the so-called normal hydrogen electrode, and that the potential of this electrode shall be called zero.[1] Since this is our ultimate standard and since it

[1] The Gibbs-Helmholtz equation is

$$T\frac{dE}{dT} = E + \frac{\Delta H}{nF}$$

where E, T, n and F have their customary meanings and ΔH is the increase in heat content (see page 238). If, instead of applying this to the whole

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is not permitted to employ any of the ordinary equations except
at constant temperature, we must add the specification that the
potential of this electrode is to be zero at all temperatures.
However, we must operate with some material system the
hydrion activities of which are known at different temperatures
or are assumed to be the same within moderate variation of tem-
perature.

It will be made plain in Chapter XXIII that it is a very difficult
matter to determine the hydrion activity of any actual solution
which is to be used as an original standard. Nevertheless, this
must be done if there is to be maintained a consistent use of the
equation

$$- E_h = \frac{RT}{F} \, ln \, \frac{1}{(H^+)}$$

Imagine, for the sake of the argument, that tenth molar hydro-
chloric acid solution is to be the original standard and that
$(H^+)_{25}$ is determined for one temperature, 25°C. Strictly $(H^+)_{30}$,
the hydrion activity of this particular solution at 30°C. might be
different. Then it would be necessary to repeat at 30° the method
used in reaching the value at 20°.

However, there are three justifications for regarding the hydrion
activity in a dilute hydrochloric acid solution to be fairly con-
stant within moderate ranges of temperature. The Debye-
Hückel theory indicates that at high dilution the activity coeffi-
cient should not change greatly with change of temperature.
(See page 500.) Experimental values of the heat of dilution are
very small up to 0.1 M. Various measurements of the colligative
properties indicate that the change is small. For these reasons
the assumption of constant hydrion activity of a dilute hydro-
chloric acid solution has entered estimates of various tempera-
ture coefficients, notably that of the potential of the tenth normal
calomel half-cell.

Before discussing specific cases it may be emphasized that we
are not at all concerned with the absolute temperature coefficient

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cell, we write it for the normal hydrogen half-cell and define $E = 0$ and $\frac{dE}{dT}$
$= 0$, it follows that $\Delta H = 0$. That is, the change in heat content of the
normal hydrogen half-cell is zero by definition.

of any single electrode potential.   Since there is no way of measuring a single electrode potential, it has been convenient to introduce the definition that the standard selected shall be zero.   Since none of the ordinary equations applies to systems which are not in thermal equilibrium we have no fundamental interest in measuring the difference of potential between two half-cells of the same composition, each at a different temperature.   Therefore, there is added the specification that the standard potential shall be zero at all temperatures.   There is a still more pertinent reason for lack of interest in this latter type of experiment.   We have difficulties enough with liquid junctions without introducing the large potentials at liquid junctions in a temperature gradient.

The confusion in the subject should be apparent if we now state that measurements with cells not at thermal equilibrium frequently have been introduced in discussions of temperature coefficients of quantities applying to our subject.   Furthermore, in several of these discussions the "normal hydrogen electrode" itself has been given a temperature coefficient.   Thus Sørensen and Linderstrøm-Lang (1924) say ". . . . the hydrogen electrode, with an electrode liquid 1 N with regard to hydrogen ions, has a temperature coefficient of almost the same magnitude as the 0.1 normal calomel electrode . . . . " also they say " . . . . it seems to us hardly practical, in the definition of π_0 (potential of normal hydrogen electrode) to introduce as Clark[2] has done the supposition that the potential between hydrogen platinum electrode and the 1N hydrogen ion solution should be taken as nil at all temperatures, since the whole temperature coefficient of the cell[3] would thus fall upon the calomel electrode, the true temperature coefficient of which is as mentioned above, quite different from that of the cell."

Also Kolthoff and Tekelenburg (1926) say " . . . . the potential of the N hydrogen electrode increases with the temperature."   Compare also Kolthoff and Furman (1926) and Mislowitzer (1928).

Since the problem necessitates the *definition* of some standard of reference, there seems to be no fundamental reason why various schemes cannot be devised for dealing with the temperature coefficients of cells.   However, I have failed to find, either in the treatment by Sørensen (1912), Sørensen and Linderstrøm-Lang (1924) or in the treatment by Kolthoff and Tekelenburg (1927), a precise definition of the problem.   I shall, therefore, refrain from joining them in this matter and shall use Lewis' (1914) definition.   This is, I believe, the custom in the treatment of cells not

[2] It was Lewis (1914) who specified that the "normal hydrogen electrode" shall be considered as having zero potential at all temperatures.

[3] Referring to the cell Pt, H_2 | H^+ (1M) | KCl, HgCl | Hg.

concerned in pH measurements. Furthermore, I must confess inability to trace the manner in which either Sørensen and Linderstrøm-Lang or Kolthoff and Tekelenburg have utilized their measurements of cells not in thermal equilibrium. It appears to me that in the end the determinative measurements they made were of cells in thermal equilibrium and that the hydrion activity of some definitive material solution was either calculated or assumed to be the same at different temperatures. The potential of a hydrogen electrode in any material solution other than that which maintains unit activity will of course have a temperature coefficient within the meaning of the definition adopted.

TEMPERATURE COEFFICIENT FOR THE CALOMEL HALF-CELL

Lewis and Randall (1914) give the following method of determining the temperature coefficient for the tenth-normal KCl calomel half-cell.
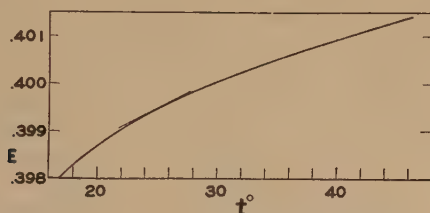
FIG. 81. ELECTROMOTIVE FORCES, E, AT TEMPERATURES t°C. FOR THE CELL
$-Pt, H_2$ (1 atmos.) | HCl (0.1 M), HgCl | Hg+

Figure 81 depicts the change of potential of the cell

$$-Pt, H_2 \mid HCl\ (0.1\ M),\ HgCl \mid Hg+ \qquad\qquad I$$

when, *in each case at constant temperature*, the potentials of the cell are measured at different temperatures.

The data led Lewis and Randall (1914) to the empirical equation

$$E_I = 0.0964 + 0.001881\ T - 0.000,002,90\ T^2 \qquad (1)$$

Differentiation of (1) gives

$$\frac{dE_I}{dT} = 0.001,881 - 0.000,005,80\ T \qquad (2)$$

As was stated before, the temperature coefficient of the potential of the half-cell

$$\text{Pt, H}_2^{'} \mid \text{HCl (0.1 M)}$$

should, in strictness, be determined experimentally (by some procedure such as is outlined in Chapter XXIII). However, in the absence of adequate data, Lewis and Randall assume that for moderate changes of temperature the hydrion activity in 0.1 M HCl will remain a constant, C. The potential of this half-cell is given by

$$E_h = 0.000,198,322 \text{ T log C} \tag{3}$$

Lewis and Randall used for E_h the value -0.0684 at $25°$. Introduce $E_h = -0.0684$ and $T = 273.1 + 25$ into (3) and solve for log C. This gives: log C $= -1.15696$. Introduce this value in (3) and differentiate to obtain:

$$\frac{\Delta E_h}{\Delta T} = -0.000229 \tag{4}$$

This is the temperature coefficient of the potential at the platinum electrode of cell I, the over-all temperature coefficient of which is given by equation (2). Consequently 0.000229 must be subtracted from the right of equation (2) to yield in (5) the temperature coefficient of the calomel half-cell with 0.1 M HCl. We shall round off the numbers and use:

$$\frac{d\mathbf{E}}{dT} = 0.00165 - 0.000,005,80 \text{ T} \tag{5}$$

Lewis and Randall assume that (2) will apply also to the cell

$$- \text{Pt, H}_2 \mid \text{HCl (0.1 M)} \parallel \text{KCl (0.1 M), HgCl} \mid \text{Hg+} \qquad \text{III}$$

Consequently (5) gives the temperature coefficient of the half-cell

$$\parallel \text{KCl (0.1 M), HgCl} \mid \text{Hg} \qquad \text{IV}$$

Equation (5) is the differential of (6)

$$E_c = E_{oc} + 0.00165 \text{ T} - 0.000,002,90 \text{ T}^2 \tag{6}$$

E_{oc} can be found by taking either Sørensen's value $E_c = 0.3380$
for 18°C. or the value 0.3353 at 25° from table 61 (see page 472).
Then the values of E_c at different temperatures may be calcu-
lated.

In Chapter XXIII are presented arguments leading to the use
of a standardized value for the standard half-cell:-

$$|| \text{ KCl (sat.) } | \text{ KCl (0.1 N), HgCl } | \text{ Hg} \qquad \text{V}$$
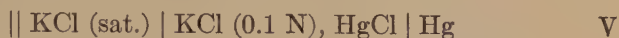
Assuming that the temperature coefficient of half-cell IV applies
to the standard half-cell V and adopting Sørensen's value for

TABLE 57

Values of calomel half-cells at different temperatures

Half-cell IV || KCl (0.1 M), HgCl | Hg
Half-cell V || KCl (sat.) | KCl (0.1 N), HgCl | Hg
Half-cell VI || KCl (0.1 N) | KCl (1.0 N), HgCl | Hg

	HALF-CELL IV USING 0.3353 AT 25°	HALF-CELL V (SØRENSEN) CALCULATED	HALF-CELL V (SØRENSEN) FOUND	HALF-CELL VI (SØRENSEN BASIS)
°C.				
18	0.3357	**0.3380**	**0.3380**	0.2865
20	0.3356	0.3379	0.3378	0.2860
25	**0.3353**	0.3376		0.2848
30	0.3348	0.3371	0.3370	0.2835
35		0.3365		
38	.	0.3361		
40	0.3335	0.3358	0.3359	
50	(0.3315)	(0.3338)	0.3344	

18° as a point of reference, we obtain the values for the standard
half-cell V shown in table 57.

For the cell

$$- \text{ Hg } | \text{ HgCl, KCl (1.0N) } | \text{ KCl (0.1N), HgCl } | \text{ Hg } +$$
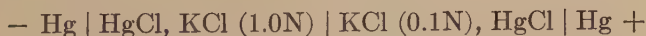
the author finds at 20° 0.0519, and at 30° 0.0536. Interpolation
between these values on the assumption that the E. M. F. is a
linear function of the temperature gives an E. M. F. at 25°
which is within 0.15 millivolts of that found by Lewis, Brighton
and Sebastian for a similar cell with molal and 0.1 molal KCl
and a linear temperature coefficient of 0.000,17. Sauer's value

at 18° is 0.0514 and that of Fales and Vosburgh at 25° is 0.0524. Neither of these values falls in with those mentioned above but when taken by themselves and with the 15° value, 0.0509, given in the footnote of the paper by Fales and Vosburgh (1918) they furnish a temperature coefficient of the same order.

With these data we can calculate the value of the half-cell

$$\| \text{KCl (0.1 N)} \mid \text{KCl (1.0 N), HgCl} \mid \text{Hg} \qquad \text{VI}$$

from the standardized value of the "tenth normal" calomel half-cell.

For the potential of the saturated KCl calomel half-cell Michaelis (1914) gives values at different temperatures which are not quite a linear function of temperature. Vellinger (1926) finds a linear relation. Neither author gives all the details of the method of reference. Fales and Mudge (1920) report potentials at different temperatures for the cell

$$-\text{Pt, H}_2 \mid \text{HCl (0.1 M)} \mid \text{KCl (sat.), HgCl} \mid \text{Hg} +$$

The temperature coefficient of this cell was *almost* linear. If, as was done in calculating the temperature coefficient for the 0.1 N KCl calomel half-cell, we assume that the potential of the hydrogen electrode in 0.1 M HCl becomes more negative by 0.00023 volts per degree increase of temperature we calculate from the data of Fales and Mudge the following approximate temperature coefficients.

$$\frac{d\text{E}}{dt} = -0.000{,}788 \text{ between 25° and 40°}$$

$$\frac{d\text{E}}{dt} = -0.000{,}695 \text{ between 40° and 60°}$$

$$\frac{d\text{E}}{dt} = -0.000{,}75 \quad \text{between 25° and 60° by best curve}$$

A best straight line through Michaelis' data gives $-0.000{,}761$. Vellinger gives $-0.000{,}66$.

Fales and Mudge (1920) give only their value at 25° as reliable[4] for the potential between the 0.1M calomel half-cell and

[4] They did not adequately protect their half-cells from interdiffusion.

the saturated calomel half-cell. They report as the average of 36 cells 0.0918±0.0002. If we use 0.3376 for the half-cell

$$\| \text{ KCl (sat.) } | \text{ KCl (0.1 N), HgCl } | \text{ Hg}$$

we obtain 0.2458 ± 0.0002 for the half-cell[1]

$$\| \text{ KCl (sat.), HgCl } | \text{ Hg}$$
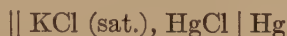
This is practically the same as the value 0.2457 for 25° reported by Vellinger, 0.2458 (0.2460 corrected to our value for the tenth normal) reported by Michaelis and 0.2454 Scatchard (see page 470). We shall use 0.2458 at 25° as an orienting value.

The several temperature coefficients are not in adequate agreement for the satisfactory calculation of values for other temperatures. If, however, we use $\frac{d\mathbf{E}}{dt} = -0.000,76$ (the average of Michaelis' and Fales and Mudge's values for the lower temperatures) we obtain the values of the following table.

TABLE 58
Tentative values for the cell
$\| \text{ KCl (sat.), HgCl } | \text{ Hg}$

t	E	t	E
18	0.2511	30	0.2420
20	0.2496	35	0.2382
25	**0.2458**	38	0.2359
		40	0.2344

At 38° the value in the table is 0.0013 volt lower than that of Vellinger and 0.0009 volt higher than that of Michaelis.

Tentatively it will be wise to use the above values as approximations and to standardize each saturated half-cell as used.

It is interesting to note that the saturated calomel half-cell has a large temperature coefficient and, by reason of its nature, is especially subject to hysteresis. Temperature *fluctuations* therefore jeopardize accurate measurements. On the other hand the potential of a cell composed of a hydrogen or quinhydrone half-cell and a saturated KCl calomel half-cell has a small temperature coefficient so that, if constant temperature prevail, the

temperature value may be in considerable error without causing great error in the potential. The error then incident to the mistaken temperature lies in the use of the wrong temperature factor.

TEMPERATURE COEFFICIENTS FOR BUFFER SOLUTIONS

In the standardization of buffer solutions, cells of the type given below were used directly or indirectly by Sørensen (1909), Clark and Lubs (1916), Walbum (1920) and others.

$$- \text{ Pt, H}_2 \text{ (1 atmos.)} \left| \begin{array}{c} \text{Buffer} \\ \text{Solution} \\ \text{A} \end{array} \right| \begin{array}{c} \text{KCl} \\ \text{(sat.)} \\ \text{B} \end{array} \left| \begin{array}{c} \text{KCl} \\ \text{(0.1 N)} \\ \text{C} \end{array} \right|' \text{HgCl} \left| \begin{array}{c} \text{Hg} + \\ \text{D} \end{array} \right.$$
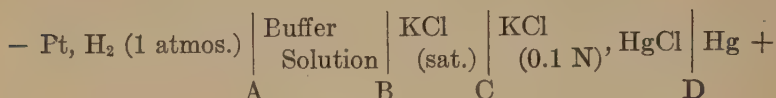
If, at a given temperature, the electromotive force of the cell is measured, the potential at A is readily calculated when the potential of the half-cell

$$|| \text{ KCl (sat.)} | \text{ KCl (0.1 N), HgCl} | \text{ Hg}$$
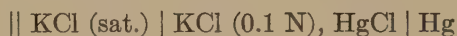
at the given temperature is known and the potential of B is zero.

In Chapter XXIII it will be recommended that variation of the potential at B be neglected and that the algebraic sum of the potentials at B, C and D be regarded as the potential of the so-called tenth normal calomel electrode as it has been applied in these instances. The previous section gives the standardized values of this half-cell at various temperatures.

This procedure standardizes an arbitrary method of computing the potential at A.

The so-called pH-values of buffer solutions are calculated from the relation

$$\text{pH} = \frac{- \text{ potential at A}}{0.000,198,322 \text{ T}}$$

This gives a definite methodical meaning to pH values. The pH values of any given buffer solution at stated temperatures must then be determined experimentally by the standardized procedure. Such *essentially* is the procedure followed by Walbum. His values are found in Chapter IX.

Kolthoff and Tekelenburg (1927) have stated an extensive

TABLE 59

Kolthoff and Tekelenburg's data for pH values of buffers at different temperatures

BUFFER	TEMPERATURE	pH (HYDROGEN ELECTRODE SERIES)
	°C.	
0.1 M acetic acid	25	4.60
0.1 M sodium acetate	40	4.61
	50	4.63
Mono sodium citrate 0.1 M	18	3.66
	30	3.65
	40	3.65
	50	3.66
	60	3.65
Di sodium citrate 0.1 M	20	4.96*
	30	4.96
	40	4.96
	50	4.97
Acid potassium phthalate 0.05 M	18	3.92
	30	3.92
	40	3.93
	50	3.94
	60	3.94
Sørensen's "citrate 4.45"	18	4.45
	30	4.43
	40	4.41
	50	4.40
	60	4.40
Sørensen's "Glycine—HCl 2.28"	18	2.26
	30	2.25
	40	2.25
	50	2.25
0.15 M Na_2HPO_4	25	11.29
0.1 M NaOH	40	11.08

* Compare Walbum. See page 211.

series of pH values for various buffer mixtures at different temperatures. They state that they "have made a thorough investigation" of the temperature coefficients of "the hydrogen- and quinhydrone electrodes" but the details are contained in Tekelenburg's dissertation (1926) and have not been available to me. It appears that although they give an extensive discussion of the absolute temperature coefficients of various half-cells, measured without thermal equilibrium of the cell as a whole, Kolthoff and Tekelenburg assumed pH 2.038 as the value of 0.01 N HCl + 0.09 N KCl at all temperatures (?).

As already indicated a similar assumption of the constancy of the hydrion activity of a hydrochloric acid solution entered Lewis' derivation. It is, therefore, not improbable that the data of Kolthoff and Tekelenburg finally are in terms of the system here recommended so far as temperature coefficients are concerned.

Representative data from their paper are given in table 59.

By reason of a departure from usual methods of standardization Kolthoff and Tekelenburg's pH values are somewhat lower than usual. This should not affect the temperature coefficients.

Hastings and Sendroy (1924) have obtained the data for phosphate solutions at 20° and 38° which are tabulated on page 212.

TEMPERATURE COEFFICIENTS OF INDICATOR CONSTANTS

In the older literature very little was said of the effect of temperature variation.

Kolthoff (1921) has extended the theory of Schoorl in which account is taken of the acidic or basic nature of an indicator, but there often remains some question as to how a given indicator is to be classified. Kolthoff, using the values of Kohlrausch and Heydweiller for the dissociation constant of water at various temperatures, has reduced his observations to the following table. In this table the displacement of −0.4 for the thymol blue means that if thymol blue in a solution at 70°C. shows the same color as the same concentration of this indicator in a buffer of pH 9.4 at ordinary temperature then the pH of the solution at 70°C. is 9.0. Corrections for temperatures between room

temperature and 70°C. may be interpolated from the data in the table.

In determining their temperature coefficients for indicator constants Michaelis and Gyemant (1920) (see page 129) assumed constancy in the pH of acetate buffers used with p-nitrophenol In the study of m-nitrophenol they used phosphate buffers to the pH values of which they ascribed a temperature coefficient based on the work of Michaelis and Garmendia. They also used a

TABLE 60

Displacement of indicator exponent between 18°C. and 70°C. after Kolthoff

INDICATOR	pH DISPLACEMENT	pOH DISPLACEMENT	RATIO OF DISSOCIATION CONSTANT AT 70°C. TO THAT AT ORDINARY TEMPERATURE
Nitramine.....................	-1.45	0.0	1.0
Phenol phthalein..............	-0.9 to 0.4	-0.55 to 1.05	About 5
Thymol blue, alkaline range...	-0.4	-1.05	2.5
α-naphthol phthalein..........	-0.4	-1.05	2.5
Curcumine....................	-0.4	-1.05	2.5
Phenol red...................	-0.3	-1.15	2.0
Neutral red..................	-0.7	-0.75	
Brom cresol purple............	0.0	-1.45	1.0
Azolitmin....................	0.0	-1.45	1.0
Methyl red...................	-0.2	-1.25	
Lacmoid......................	-0.4	-1.05	2.5
p-nitro phenol................	-0.5	-0.95	3.2
Methyl orange.................	-0.3	-1.15	14.0
Butter yellow.................	-0.18	-1.17	15.0
Bromphenol blue..............	0.0	-1.45	1.0
Tropaeolin OO................	-0.45	-1.0	10.0
Thymol blue, acid range.......	0.0	-1.45	1.0

temperature coefficient for borate buffers in determining, for instance, the temperature coefficients for salicyl yellow. The original articles must be consulted for the somewhat involved detail.

Hastings and Sendroy (1924) and Hastings, Sendroy and Robson (1925) have systematized the Gillespie method as applied by Cullen (1922), see also Austin, Stadie and Robinson (1925). They determined anew the pH values of phosphate buffers (see

page 212) at 20° and 38° and of acetate buffers at 20°. In the latter case they assumed no change of pH with change of temperature to 38°C. In these standardizations 0.1 N HCl with assigned value of pH 1.08 was employed. They obtain the pK′ values of the following table:

Indicator exponents at different temperatures

INDICATOR	pK'_{20}	pK'_{38}
Phenol red.	7.78	7.65
Brom cresol purple............................	6.19	6.09
Chlor phenol red.....	6.02	5.93
Brom cresol green.............................	4.72	4.72

Compare these with values of table 11, page 94. See figure 18, page 103.

TEMPERATURE COEFFICIENTS OF OTHER EQUILIBRIUM CONSTANTS

In the older literature are to be found numerous measurements of the temperature coefficients of acid and base dissociation constants. These were based upon conductivity, for the most part. Extensive data are assembled by Scudder (1914) and in Landolt-Börnstein's Tabellen (1923).

See page 45 for estimates of K_w at different temperatures.

TEMPERATURE COEFFICIENTS OF QUINHYDRONE ELECTRODE POTENTIALS

See page 419.

CONCLUSION

At the present time the lack of sufficiently extensive systematic data has made necessary various and divers assumptions by different authors who have dealt with the temperature coefficients of the quantities briefly treated in this chapter. By reason of the variety of these assumptions and, in many cases, the lack of sufficiently specific detail, it is impracticable to systematize the existing data. The operator must choose his system and should state in detail the assumptions he makes.

CHAPTER XXIII

Standardization of pH Measurements

If there is a service which philosophy can render with more advantage to science than any other, it is probably to keep reminding men of science never to forget to criticise their categories before employing them.—Viscount Haldane.

In the development of the theory of electrolytic dissociation the hydrogen electrode came upon the scene comparatively late and after many of the quantitative relations had been outlined by conductance data. It was, therefore, natural that these data should have been accepted in the standardization of potentiometric measurements. It now appears that the interpretation of conductance data is more complicated than at first supposed and that certain of the values that have been used in the standardization of potentiometric measurements are in doubt. Also, it is now recognized that the hydrogen cell does not directly give information upon relative hydrion *concentrations*. The resulting confusion demands careful consideration.

Let us review briefly the way in which conductance data entered the standardization of potentiometric measurements.

Assume, first, the validity of the ideal gas laws. Then the following equation relates the electromotive force of a hydrogen cell to the concentrations of hydrions in solutions 1 and 2, provided the hydrogen partial pressure is the same at each electrode.

$$\text{E. M. F.} = \frac{\text{R}T}{\text{F}} \, ln \, \frac{[\text{H}^+]_1}{[\text{H}^+]_2} \tag{1}$$

By use of this relation one can determine in the first instance only the *ratio* of two hydrogen ion concentrations. If the value of either $[\text{H}^+]_1$ or $[\text{H}^+]_2$ is to be found, the value of the other must be known. Conductance data have been relied upon to furnish one known.

Likewise, when there is used a cell composed of a calomel half-cell and a hydrogen half-cell, the value assigned to the calomel

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half-cell is such that, when it is subtracted from the total E.M.F. of the cell, the resulting E.M.F. is as if between a normal hydrogen electrode and the hydrogen electrode under measurement. This implies the experimental determination of the difference of potential between a *normal* hydrogen electrode and the calomel electrode or else between the calomel electrode and a hydrogen electrode in some solution of *known* hydrogen ion concentration. To determine this known hydrogen ion concentration conductance data upon hydrochloric acid solutions have been relied upon.

Only when some standard of reference is agreed upon, can $[H^+]_1$, of equation (1), be set at unity and the equation written:

$$\frac{\text{E. M. F.} \times \mathbf{F}}{2.3026\ \text{RT}} = \log \frac{1}{[H^+]} = pH \tag{2}$$

or

$$\frac{\text{E. M. F.}}{0.000,198,322\ \text{T}} = pH \tag{2a}$$

The principle which was assumed in the use of the conductivity method may be described briefly as follows.

With a given potential gradient between two fixed electrodes, the current carried by the ions in the solution should be a direct function of the number of equivalents of ions and of the speeds of their ionic migrations. If, independent of the dilution, each of the several kinds of ions has its fixed migratory speed under the given potential gradient, the current becomes a measure of the number of equivalents of carrying ions. Suppose then that the solution has been diluted until its solute, an ionogen acid, has attained complete dissociation. Further dilution does not increase the *proportion* of ions to total acid and the current, per equivalent of acid, per unit volume, under the given conditions, becomes constant. While complete dissociation was not supposed to occur until infinite dilution was reached, we shall assume that the means of extrapolating to this condition were adequate. Then for a simple acid, of type HA, the ratio of equivalent conductance at a given concentration, to the equivalent conductance at infinite dilution should give α, the degree of dissociation.

It is then a simple matter to calculate the hydrogen ion concentration.

We have already noted that attempts to apply this idea of progressive ionization to strong acids in solution rested upon a misconception of the nature of strong acids. But in addition there is the view, outlined in Chapter XXV, that, although ions in solution may be regarded as free and separate entities in the sense that they have departed from *fixed* combinations in their ionogens, they are still subject to an interionic force. On dilution the effect of this becomes less. Under the stress of an electric field the ion groups become distorted and the fields between them and the solvent molecules change from point to point of the migration. The energy involved varies with the density of the ion atmosphere (i.e., with dilution) and enters the formulation of conductance in a complicated manner. It appears as if the ions of a given kind have migratory speeds which vary with the composition (e.g., dilution) of the solution. Therefore, one of the important postulates of the classical theory fails. Jahn (1900) and Lewis (1912) long ago noted the discrepancies and expressed them as the failure of the postulate of constant migratory speed. For a discussion of the matter in terms of Debye's treatment see Debye (1927) and Onsager (1927) (see references under Faraday Society).

The remodeling of the theory of conduction in solution has left open to serious doubt the older values for hydrogen ion concentrations in specific solutions.

But let us suppose that adequate methods are available for determining the hydrogen ion concentration of some solution to be used as a standard for hydrogen electrode comparisons. Is the problem solved? It is not. It will be recalled that the potentiometric method, employed in the use of the hydrogen electrode, measures the free energy of transport of hydrogen ions between two solutions. There is no simple, general relation between this free energy change and the corresponding change in concentration. As explained in Chapter XI, solutions of different composition have different constraints upon the ease with which hydrogen ions may be removed. This necessitates the inclusion of a correction term specific for each member of a pair of solutions when the energy equation for a "concentration" cell is formulated in the classical manner.

The more extensive and accurate data which bear upon our subject are those obtained with solutions of hydrochloric acid. But both experiment and the Debye-Hückel equation show that the correction cannot be eliminated in the range of concentration of hydrochloric acid solutions within which it is practicable to operate. In other words it is impossible in the first instance to calculate a definite electrode potential by reference alone to a unit concentration of HCl. We have to console ourselves with the remembrance that the correction disappears only at infinite dilution. The problem then is to establish a substantial basic datum with that somewhat unsubstantial hydrochloric acid solution of zero concentration! Obviously the only way this can be done is to extrapolate some function to the condition of zero concentration. How this is done and what function is used will appear presently.

By way of *illustration* one of many routes will now be followed to specifications which could serve in the standardization of pH measurements.

Consider the cell:

$$- \text{ Pt, } \text{H}_2 \mid \text{HCl, AgCl} \mid \text{Ag} +,$$

namely a hydrogen electrode and a silver-silver chloride electrode both in contact with the same solution of hydrochloric acid. Since no appreciable liquid-junction potential is concerned and since the silver-silver chloride electrode is probably better than the calomel electrode for use with the hydrogen electrode in acid solution, there is a distinct advantage in considering this cell first.

At the hydrogen electrode the single potential difference may be formulated by equation (3) where a constant, E'_H, is included because no standard of potential-difference has yet been defined.

$$\text{E}_\text{H} = \text{E}'_\text{H} + \frac{\text{RT}}{\text{F}} \, ln \, \frac{[\text{H}^+]}{\sqrt{\text{P}}} + \text{V}_\text{H} \qquad (3)$$

V_H is a variable correction introduced to allow for the failure of the classical equation.

At the silver electrode the potential difference may be formulated in its lowest terms by:

$$\text{E}_\text{Ag} = \text{E}'_\text{Ag} - \frac{\text{RT}}{\text{F}} \, ln \, [\text{Cl}^-] - \text{V}_\text{Ag} \qquad (4)$$

Here again a variable correction, V_{Ag}, is introduced to allow for the failure of the classical equation which is based on the ideal gas laws.

At unit hydrogen pressure, when $P = 1$, we have for the cell as a whole (silver positive to platinum):

$$\mathbf{E}_{Ag} - \mathbf{E}_H = \mathbf{E}'_{Ag} - \mathbf{E}'_H - \frac{RT}{F} \, ln \, [H^+] \, [Cl^-] - V_{Ag} - V_H \quad (5)$$

In accord with a rather widely accepted conclusion we shall now assume that hydrochloric acid is completely dissociated within the range of concentration to be considered. Then

$$[H^+] \, [Cl^-] = [HCl]^2$$

where [HCl] represents simply the analytical concentration of hydrochloric acid without specification of its state.

Introducing this assumption and using the numerical form of the equation for 25°C., we have

$$\mathbf{E}_{Ag} - \mathbf{E}_H = \mathbf{E}'_{Ag} - \mathbf{E}'_H - 0.11824 \log [HCl] - V_{Ag} - V_H \quad (6)$$

or

$$\mathbf{E}_{Ag} - \mathbf{E}_H = \mathbf{E}'_{Ag} - \mathbf{E}'_H - 0.05912 \log [H^+] - 0.05912 \log [Cl] - V_{Ag} - V_H \quad (6a)$$

In figure 82 experimental values for $\mathbf{E}_{Ag} - \mathbf{E}_H$, as assembled by Scatchard (1925), are charted as the curve labeled A. To harmonize with a subsequent figure, the abscissa is made the square root of the molality of the hydrochloric acid solution.

If the classical equations were followed V_{Ag} and V_H of equation (6a) would each be zero. Then, if complete dissociation of hydrochloric acid were assumed, the values of [H$^+$] and [Cl$^-$] could be calculated from the known molality of the hydrochloric acid solution. Then, since $\mathbf{E}_{Ag} - \mathbf{E}_H$ has been determined in each instance, the equation can be solved for $\mathbf{E}'_{Ag} - \mathbf{E}'_H$. This constant value should determine the level of a line such as that shown in figure 82 at 0.2226 volts. Line B. It is evident that $\mathbf{E}'_{Ag} - \mathbf{E}'_H$, when so calculated by neglect of V_{Ag} and V_H, furnishes data which do not conform to this reference line at 0.2226.

Since the corrections disappear at infinite dilution, a curve drawn through the blackened cycles should meet the desired

base line at $M = 0$. The problem is thus resolved into the diffi-
cult task of extrapolating this to $M = 0$ or $\sqrt{\mu} = 0$.

To this problem we shall revert presently. For the moment
assume that the extrapolation has been carried out correctly and
that the intersection has been found to be at 0.2226 volt. This is
value of $E'_{Ag} - E'_{H}$ in equation (6). Now introduce the *defini-*
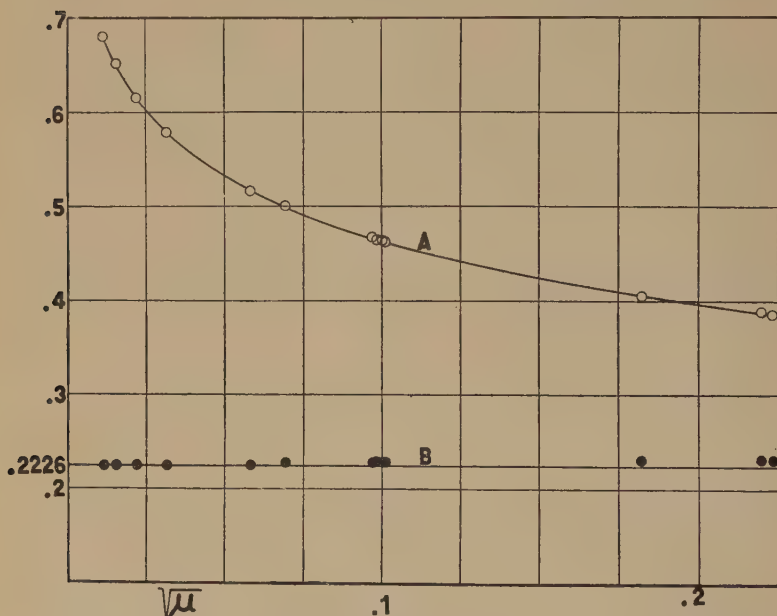
FIG. 82. CURVE A: ELECTROMOTIVE FORCE E AT VARIOUS VALUES OF
$\sqrt{\mu}$ FOR THE CELL

Pt, H_2 (1 atmos.) | HCl (X), AgCl | Ag

$\sqrt{\mu} = \sqrt{\text{molality of HCl}}$.   Curve B: $E_{Ag}' - E_{H}'$.

tion of the normal hydrogen electrode given on page 257; but,
for the convenience of the present purpose, recast the definition
to the following. The normal hydrogen electrode shall have a
single potential difference of zero when the hydrogen pressure is
one atmosphere and the concentration of hydrogen ions is such
that

$$\frac{RT}{F} \, ln \, [H^+] + V_H = 0$$

As a result of this definition it will be seen from equation (3) that E'_H is zero by definition. Consequently the value of E'_{Ag} $- E'_H$ in (6) is the value of E'_{Ag}, namely the constant of the silver-silver chloride electrode, referred to the defined hydrogen standard of potential.

Now let us return to the extrapolation of the curve through the points shown in figure 82 by blackened circles. For this purpose the curve will have to be made on larger scale. See figure 83. Extrapolations to M = 0 have been made with the aid of empirical curve-fitting or empirical equations. Thus Linhart (1917),
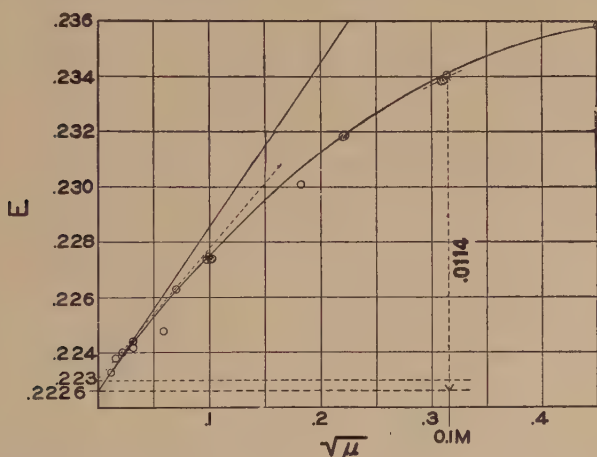
Fig. 83. Corrections at Various Values of $\sqrt{\mu}$ for the Constant of the Cell

$-$Pt, H_2 (1 atmos) | HCl, AgCl | Ag$+$
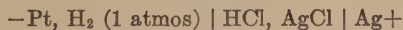
whose admirable data are those falling closest to M = 0, extrapolated to 0.2234. Scatchard (1925), however, gives to Linhart's last point more weight than Linhart allows. He also uses as guides to his own extrapolation the Debye-Hückel equation[1] both in its simplest reduced form to give the tangent shown, and, in a more extended form, to pick up the departure from this tangent at the points for the higher concentrations. By these

[1] Chapter XXV.

means Scatchard finds the intersection with the ordinate $M = 0$, to be at 0.2226 volt.[2]

For present purposes we shall use Scatchard's value 0.2226 volt for the electromotive force of the cell:

$$Pt, H_2 \mid HCl, AgCl \mid Ag$$

which would obtain were [HCl] = 1 and were there no correction terms. In other words it is the electromotive force when the activity is unity, i.e., (HCl) = 1.[3]

Returning now to the experimental data for the real cell with 0.1 M HCl, we might assume that the correction, $(-V_{Ag} - V_H) = 0.0114$ (see fig. 83) could be equally divided between V_{Ag} and V_H. This would be equivalent to assuming the activity coefficients of the hydrion and chloride ion to be equal to one another. On this basis we obtain

$$0.2226 + 0.05912 + 0.00570 = +0.2874$$

for the silver chloride half-cell with 0.1 M HCl and

$$0 - 0.05912 - 0.00570 = -0.0648[4]$$

for the hydrogen half-cell with 0.1M HCl. Although the above assumption will later be rejected, we might use the value -0.0648 for the hydrogen half-cell with 0.1 M HCl and consider this our standard. However, if we were to join this half-cell with other miscellaneous half-cells, we would encounter the difficulty of varying liquid junction potential. As explained in Chapter XIII the magnitude of the liquid junction potential is greatly reduced when one side is a saturated solution of potassium chloride. For this reason it is usual, in miscellaneous measurements, to form a cell in which saturated KCl solution forms a bridge. Were the

[2] LaMer (1927) has criticized Scatchard's employment of the Debye-Hückel equation in this extrapolation. However, it will presently become clear that there is no occasion for our attempting here to resolve this difference of opinion or to enter a detailed discussion of the comparison between Scatchard's data and those of Nonhebel and of Randall and Vanselow to which LaMer refers. There has just come to hand Randall and Young's paper in which the value is lowered to 0.2221.

[3] The reader is again reminded that () is used to indicate activity while [] is used to indicate concentration.

[4] This corresponds to pH = 1.096.

calomel half-cell with saturated KCl considered by all to be a safe, permanent standard of reproducible qualities, we might consider alone the comparisons of this half-cell with the hydrogen half-cell discussed above. It is preferable to seek the value of the more reproducible "tenth normal" calomel half-cell. Scatchard proceeds as follows.

He used the arrangement

$$\text{Hg} \mid \text{HgCl, KCl (sat.)} \Big\} \begin{matrix} \text{HCl } (\mathbf{X}), \text{ AgCl} \mid \text{Ag} \\ \text{A} \end{matrix}$$
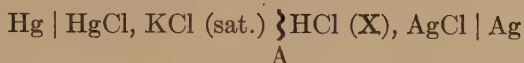
and varied X. A flowing junction was used at A. The equation may be written:

$$\mathbf{E_{obs}} = \mathbf{E'_c} - \mathbf{E'_{Ag}} - 0.05912 \log [\text{Cl}^-] - V_{Ag} - V_L. \quad (7)$$

where $\mathbf{E'_c}$ is the constant potential at the mercury, $\mathbf{E'_{Ag}}$ is the constant, 0.2226 volt (see above), characteristic of the silver-silver chloride electrode discussed previously, V_{Ag} is the correction for the silver-silver chloride electrode and V_L is the variable potential at junction A.

The data can be treated graphically in a manner quite comparable with that used in the former case. Scatchard made the extrapolation with the aid of the simplified Debye-Hückel equation. However, in the present instance there is a rather delicate point to watch. If the extrapolation were made purely empirically there might be obtained the value of $\mathbf{E'_c} - \mathbf{E'_{Ag}} + V_L$. Here V_L is included since the loci of the points are certainly determined by V_L in part and its value might well be *changing*. Inherent in such an extrapolation would be the conclusion that the part contributed to the value of $\mathbf{E'_c} - \mathbf{E'_{Ag}} + V_L$ by V_L *at the limit* would then be the potential of the junction saturated KCl $\Big\}$ Water. However, if, within the range of the last points nearest the tangent drawn by means of the Debye-Hückel relation, the liquid-junction potential does not vary much, the fact that the Debye-Hückel relation was used and that this has nothing to do with liquid junctions, would lead to the conclusion that the contribution of V_L is as if it were of the liquid junction potential of saturated KCl $\Big\}$ HCl in the lower experimental ranges of [HCl]. Apparently this is Scatchard's interpretation. He finds $\mathbf{E'_c} - \mathbf{E'_{Ag}} = 0.0228$ volt. $\mathbf{E'_{Ag}}$, as noted, is 0.2226. Hence $\mathbf{E'_c} + V_L$

= 0.2454 volt. This is the potential at Scatchard's saturated KCl calomel electrode including a liquid junction potential as if against 0.1 (or less) M HCl and made with flowing junction.

Instead of attempting to go to the decinormal calomel half-cell by direct comparison, Scatchard takes a route summarized as follows with the aid of figure 84.

We have already discussed the cell composed of the half-cells (3) and (8) of figure 84 (potential x). We have noted how a study of cells of this type may be made to yield the value of
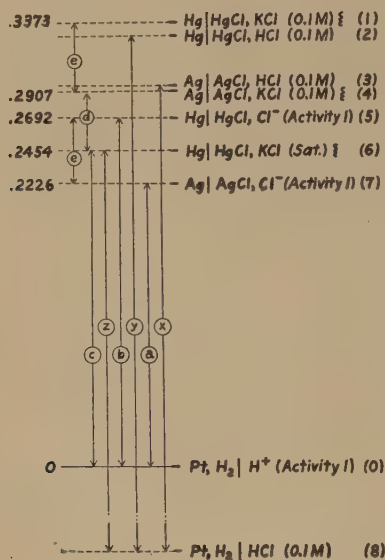
FIG. 84

Note: First steps do not require activity of Cl- but of HCl

half-cell (7) with potential (a) standardized with reference to half-cell (0) the potential at which is defined as zero. In a comparable way the cell composed of half-cells (2) and (8) (potential y) and of variations of this cell with different concentrations of HCl are made to yield the value of half-cell (5) (potential b). For this purpose Scatchard uses the data of others for cell (2)–(8) and applies his own value for the correction term that yields the value of (5).

Next cell (6)–(8) with potential z, was treated as outlined above to reach the standardized value of (6), potential c. Experimental cell (6)–(8) possesses a junction potential, namely that of KCl (sat.) $\rangle$ HCl (0.1 M), which will be called V_{L_1}. In reaching a value for half-cell (4) by observation of potential d this junction potential, V_{L_1}, is carried along in the standardization. Also the potential of the new junction KCl (sat.) $\rangle$ KCl (0.1 M) is introduced experimentally.

The difference between b and a, that is the difference of potentential between the calomel and the silver chloride electrodes in a solution of the same chloride ion activity, is e. This same difference should apply to the cell (1)–(4). Thus the value 0.3373 for the calomel electrode with 0.1 molal KCl is reached. A correction for change from 0.1 *molal* to 0.1 *normal* brings the value to 0.3372 for the decinormal calomel electrode. There has been carried along, in the standardization, the potential of the customary junction KCl (sat.) $\rangle$ KCl (0.1 N), which should be included for practical purposes, and also a junction potential as of KCl (sat.) $\rangle$ HCl (0.1 M, or less).

If the value for the tenth normal calomel half-cell is to be obtained without those liquid-junction potentials which were carried along in the above calculations, we may take a new start with half-cell 5 (fig. 84). Introduce the estimated activity of chloride ions in 0.1 M KCl-solution. Scatchard uses 0.0762 for this activity. Whence 0.3353 is the estimated potential of the decinormal cell without liquid-junction.

In summary we have:

HCl $\rangle$ KCl (sat.), HgCl | Hg   ; $E_h = +0.2454$ at 25°
|| KCl (0.1 M), HgCl | Hg   ; $E_h = +0.3353$ at 25°
HCl $\rangle$ KCl (sat.) | KCl (0.1 N), HgCl | Hg   ; $E_h = +0.3372$ at 25°
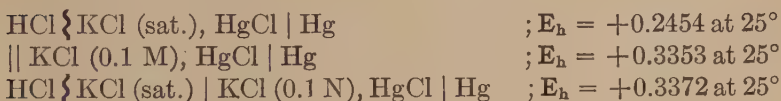
Now let us return to the problem mentioned on page 468 namely the partition of the correction between the silver chloride and hydrogen half-cells. It is a bold assumption, and one which is not in good repute, to make the even partition there used. Scatchard employs his measurements with the cell

$$\text{Hg} \mid \text{HgCl, KCl (sat.)} \rangle \text{HCl, AgCl} \mid \text{Ag}$$
$$\text{A}$$
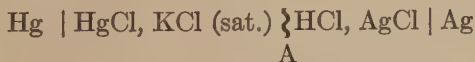
He employs the aforementioned assumptions regarding liquid junction potentials and the Debye-Hückel equation for extrapolation to zero concentration of HCl. Thereby he is able to calculate the corrections for the chloride half-cell at the several concentrations of hydrochloric acid. Having already obtained the sum of the corrections for the chloride and hydrogen half-cell, he obtains the corrections for the hydrogen half-cell.

Using activity coefficients in place of potential corrections and the relation

$$\gamma_{HCl} = \sqrt{\gamma_{H^+} \times \gamma_{Cl^-}}$$

Scatchard finds, for instance in the case of 0.1 M HCl: $\gamma_{\overline{Cl}} = 0.762$; $\gamma_{H^+} = 0.841$ and $\sqrt{\gamma_{H^-} \times \gamma_{\overline{Cl}}} = \gamma_{HCl} = 0.801$.

We have rounded off the value of γ_{H^+} to 0.84 and employ this to calculate the pH values of HCl:KCl solutions given on page 201. We also employ it to obtain those calculated potentials of the hydrogen half-cell with 0.1 N HCl which are given in table A, page 672.

TABLE 61

Some values assigned to calomel half-cells at 25°C.

Parenthesized values are calculated from unparenthesized values. Bracketed values are calculated from measurements at other temperatures.

| | HALF-CELL | |
AUTHORITY	‖ KCl (0.1M), HgCl ǀ Hg	‖ KCl (0.1M) ǀ KCl (1.0M), HgCl ǀ Hg
Beattie (1920)........................	(0.3353)	0.2826
Lewis and Randall (1921)...............	0.3351	(0.2822)
Sørensen and Linderstrøm-Lang (1924) ...	[0.3354]	(0.2825)
Scatchard (1925)......................	0.3353	(0.2826)
Average..............................	0.3353*	

* There has just come to hand Randall and Young's paper in which they give 0.3341 for the potential of the half-cell in vacuum but state that the value of the half-cell in air will be about 0.3354 by reason of an error of one to three millivolts caused by the presence of air.

It seems hardly necessary to outline other routes. That mentioned shows not only the nature of the argument but two aspects

of special interest to the purpose of this chapter. In the first
place it is evident that methods of reaching standard values are
becoming more rationalized.   In the second place there remain a
number of small discrepancies and fundamental difficulties
(especially with liquid-junction potentials) sufficient to cause
appreciable variation in the values used by different authors in
arriving at the value of any specified half-cell.   The latter fact is
obscured by the uncritical comparison in table 61.   The apparent
agreement obtains because of a remarkable cancellation of small
differences.   But even if it be granted that the average in table
61 is final, its acceptance settles only part of our problem.   Con-
sider the cell:

$$\text{Pt, H}_2 \text{ (1 atmos.)} \mid \text{solution X} \mid \text{KCl (sat.)} \mid \text{KCl (0.1 N), HgCl} \mid \text{Hg}$$
$$\qquad\quad \text{A} \qquad\qquad \text{B} \qquad\qquad \text{C} \qquad\qquad\qquad \text{D}$$

As solution X is changed there is not only a change of potential
difference at A, but there is also a change of liquid junction poten-
tial at B.   Knowledge of the potential of C + D and a measure-
ment of the whole cell is, therefore, not sufficient to give the
potential at A.   Strictly, each change of solution X will produce
a change of potential at B.   Since there is no universal rule by
which the potential at B can be calculated in each and every
case, it is necessary in practice to introduce an assumption.   Two
assumptions have been the more customary.   One is that the
junction potential at B shall be neglected.   The other is that it
shall be estimated by the Bjerrum extrapolation (see page 277),
using 3.5 M and 1.75 M KCl in place of saturated KCl solution
as bridge.

The latter assumption was used by Sørensen (1909) in deriving
the value of the "tenth normal calomel electrode" from measure-
ments of the cell

$$\text{Pt, H}_2 \text{ (1 atmos.)} \mid \text{HCl (0.1N)} \mid \text{KCl} \begin{array}{c} \text{3.5N} \\ \text{or} \\ \text{1.75N} \end{array} \mid \text{KCl (0.1N), HgCl} \mid \text{Hg}$$
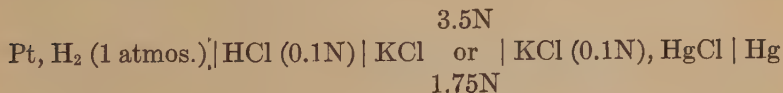
It has usually been assumed that because Sørensen used con-
ductivity data to obtain the hydrion concentration of 0.1 N HCl
and thence calculated 0.3380 (18°) for the potential of the "tenth
normal calomel half-cell" that this value must necessarily be

erroneous. As a matter of fact the Bjerrum extrapolation[5] which he used was large (74 mv.) and it appears that, by chance, he obtained a value which can still be justified. If we compare the Sørensen value at 25° (see page 453) with Scatchard's estimate for the half-cell,

$$\text{HCl} \left. \begin{matrix} \\ - \end{matrix} \right\} \underset{+}{\text{KCl (sat.)}} \underset{B}{} \underset{+}{} \underset{C}{} \left| \begin{matrix} \text{KCl (0.1 N), HgCl} \\ - \end{matrix} \right| \underset{D}{\text{Hg}}$$
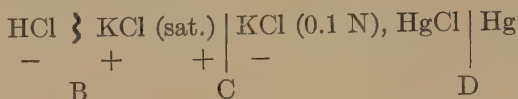
we have:

> 0.3376 (Sørensen)
> 0.3372 (Scatchard)

According to Scatchard's estimate the potential at C is 0.0027 volt with the orientation shown above and, at B, 0.0047 with the orientation shown when the solution in the hydrogen half-cell is 0.1 M HCl. (Harned (1926) calculated 0.0016.)

Since the Sørensen value, for the so called "0.1 N calomel electrode" is now frequently used as if of the above half-cell and happens to be so near to a significant value under particular circumstances, it may be considered. It is especially important to consider the Sørensen value because it has been used extensively in the standardization of buffer solutions, ionization constants and a host of miscellaneous data. The value was in substantial agreement with that recommended by Auerbach (1912) and adopted by the "Potential Commission," whence arose substantial agreement with other types of investigation. It would be quite impracticable to cite all of even the *types* of data that conform substantially to the basis established by Sørensen. Much of it is data of high accuracy and complexity. See, for example, the researches on blood and the involved carbonate equilibria.

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[5] Sørensen's average value for the cell

> Pt, H_2 | HCl (0.1 N) | KCl (3.5 N) | KCl (0.1 N), HgCl | Hg

was 0.4025 volt. His use of the Bjerrum extrapolation reduced this to 0.3975 volt. If we neglect the extrapolation and use 0.3380 volt for the potential of the tenth normal calomel half-cell, we obtain

$$\frac{0.4025 - 0.3380}{0.057732} = 1.12,$$ as the pH number of 0.1 N HCl at 18°C. in

place of Sørensen's assumed value 1.04; but this calculation is made with the use of a potential obtained with 3.5 N KCl solution, instead of saturated KCl solution, as bridge.

For *purposes of discussion* we shall use the Sørensen value 0.3376 (25°) for the half-cell

$$\text{HCl} \mid \text{KCl (sat.)} \mid \text{KCl (0.1 N), HgCl} \mid \text{Hg}$$

and 0.3353 (25°) for the half-cell

$$\| \text{KCl (0.1 N), HgCl} \mid \text{Hg}$$

Since there are only a few who retain confidence in the Bjerrum extrapolation we shall neglect it and shall continue with the assumption that saturated KCl solution is to be used. In discussing the cell

$$\text{Pt, H}_2 \text{ (1 atmos.)} \mid \text{solution X} \mid \text{KCl (sat.)} \mid \text{KCl (0.1 M), HgCl} \mid \text{Hg}$$
$$\qquad\qquad\qquad\qquad\quad \text{B} \qquad\qquad\quad \text{C}$$

the junction potential at B is to be neglected in calculations.

Undoubtedly when solution X is a phosphate solution this junction potential is much less than when solution X is a dilute hydrochloric acid solution. How much less, there is no certain way of telling. As an extreme we can consider it to compensate that at C. If so the value 0.3353 should be used for the "calomel half-cell" instead of the customary 0.3376. But if, on the dangerous assumption made above, we adopted 0.3353 for universal use, we would certainly be in error when operating with very acid solutions.

Attempts to proceed with the adoption of any fixed single value for a half-cell involving a liquid junction, the potential of which is susceptible to appreciable change as the solution under study is changed, is, of course, not strictly logical; but we are now considering arbitrary assumptions necessary to ordinary operation. In the study of phosphate buffers will the use of 0.3376 in place of 0.3353 be serious? So far as pH numbers are concerned

$$\frac{0.3376 - 0.3353}{0.05912} = 0.0389 \cong 0.04$$

gives the correction that should be added to a pH number at 25° were 0.3353 used in place of 0.3376.

But such an error is of no practical consequence in the comparison of acid-salt systems in which the acid is very weak. When $[\text{H}^+]$ is of the order of 10^{-5} or less it may be neglected in calculating the undissociated residue from $[\text{HA}] - [\text{H}^+] = [\overline{\text{A}}]$, except at impracticably high dilutions. As discussed in Chapter XXVII any standard of reference will do and our chief concern is then with agreement upon the standard selected.

A more or less uncertain but reasonable compromise may be made by allowing the error for the extreme case of the phosphate buffer where the error is of no practical importance and adopting 0.3376 which leads to substantially reasonable values in very acid solutions where $[\text{H}^+]$ is of importance not only as an index but of itself.

Possibly a sliding scale of values could be devised but in the present state of affairs this would be dangerous.

The adoption of a fixed value, which is roughly adapted to the more acid solutions and which allows an error for the extreme case where the error is of no practical importance, will doubtless lead to appreciable error in the study of *intermediate* cases.

Cohn, Heyroth and Menkin (1928) believe they detect this in their treatment of acid, acetate solutions, a discrepancy in the drift of $-\log \gamma$ being removed by the employment of 0.3357 instead of 0.3380 for measurements at 18°. They also note that, if electromotive force measurements are to be brought into harmony with recent corrected conductivity measurements of the dissociation constant of acetic acid, the value of the half-cell

$$\| \text{ KCl (sat.) } | \text{ KCl (0.1 N), HgCl } | \text{ Hg}$$
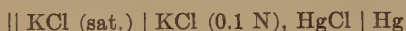
with neglect of liquid junction potential "should be between 0.3364 and 0.3370."

To what extent such adjustments will have to be made as the case is changed is a question on which I shall not even venture an opinion; but that, strictly, each individual case is a new case, in which allowance for a different junction potential must be made, can hardly be gainsaid, especially when the cases are those in which [H⁺] is high.

The use of a stated pH value for 0.1 N HCl and the use of the cell

$$\text{Pt, H}_2 \text{ (1 atmos.) } \left| \begin{array}{c} \text{HCl} \\ \text{0.1 N} \end{array} \right| \text{ KCl (sat.), HgCl } \left| \text{ Hg} \right.$$

in standardizing the saturated calomel half-cell has the appearance of being direct, simple and clear. However, it is not always certain that liquid junctions are established in a uniform manner by *different* workers and, as emphasized by Clark and Lubs (1916), the variability of potential at the junction HCl | KCl (sat.) with different methods of forming the junction makes the use of HCl dangerous for routine standardization purposes.

To illustrate the variation of present practice there may be cited a few of many bases of standardization.

Cullen, Keeler and Robinson (1925), Hastings and Sendroy (1924) and a group of American students of blood equilibria have been using pH 1.08 for 0.1 N HCl as a standardizing value with which to establish the value of a "working," saturated calomel half-cell. Neglecting liquid junction potentials, they obtain, for M/15 phosphate buffers, pH values about 0.01 unit pH greater than Sørensen's values. Hence pH 1.09, as used by Simms (1926), would leave another 0.02 pH unit to be added were the 0.04 correction mentioned above to be followed. Levene, Simms and Bass (1926) use 1.075 for 0.1 M HCl.

Sørensen and Linderstrøm-Lang (1924) in no. 10 of their recommenda-

tions advocate the use of 0.4556 volts as the extrapolated (Bjerrum) value of the following cell (presumably at 18°):

$$\text{Pt, H}_2 \text{ (1 atmos.)} \begin{vmatrix} 0.01 \text{ N HCl} \\ 0.09 \text{ N KCl} \end{vmatrix} \begin{matrix} 3.5 \text{ N KCl} \\ \text{and} \\ 1.5 \text{ N KCl} \end{matrix} \begin{vmatrix} \; \end{vmatrix} \text{KCl (0.1 N), HgCl | Hg}$$
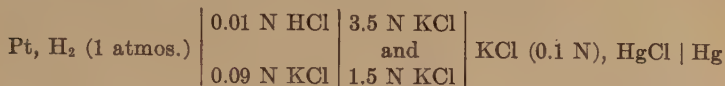
If we tentatively assume that this is also the potential of the cell

$$\text{Pt, H}_2 \text{ (1 atmos.)} \begin{vmatrix} 0.01 \text{ N HCl} \\ 0.09 \text{ N KCl} \end{vmatrix} \text{KCl (sat.) | KCl (0.1 N) HgCl | Hg}$$

and assume 0.3380 for the half-cell

$$\text{KCl (sat.) | KCl (0.1 N), HgCl | Hg}$$
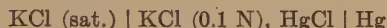
we obtain pH = 2.037. This is substantially the number, 2.04 suggested by Cullen, Keeler and Robinson (1925) for use with sat. KCl and *neglect of liquid junction*, and 2.038 by Kolthoff and Tekelenburg (1927) for use *with the Bjerrum extrapolation*. Biilmann (1927) accepts 2.029 on the basis of a personal communication from Bjerrum, and uses it with the Bjerrum extrapolation in his discussion of the quinhydrone electrode.

Other values for 0.01 N HCl $+$ 0.09 N KCl are included in the following list of contrasts.

> 2.029 Biilmann (1927)
> 2.038 Kolthoff and Tekelenberg (1927)
> 2.063 Gjaldbaek (1925)
> 2.078 Table 35a, page 201
> 2.093 Larsson (1922)

Sørensen and Linderstrøm-Lang (1927) have recently abandoned the 0.3380 value for the "tenth normal" calomel half-cell and are using 0.3357 (18°) as a basis, with intervening solution of saturated KCl and *neglect* of liquid junction. Their former (1924) general recommendations permit the Bjerrum extrapolation and their specification no. 10 provides for it in "specially accurate measurements."

Many other cases could be cited to show appreciable differences in standards.

American practice has tended toward the use of saturated potassium chloride solution as a bridge or the use of the saturated KCl-calomel half-cell as a working standard and the stated tentative assumption that the liquid junction potential shall be neglected. Many European workers still operate with the old method of extrapolation introduced by Bjerrum and with the 3.5 N KCl calomel half-cell. Although Sørensen and Linderstrøm-Lang state that the two methods give practically the same result in ordinary buffers, it is by no means certain that the two methods will lead to the same set of values when hydrochloric acid solutions of one kind or another are used as ultimate standards. Direct comparison of the results

of the two kinds of practice is beset with danger when the practical standard of reference is a hydrochloric acid solution.

In the absence of any thoroughly developed fundamental basis we may well expect in the near future as many slight but distinct differences in methods of standardization as have appeared in the recent past. Indeed it may be questioned whether any recommendation is worth while. A decision would not permit a recalculation of all important data, because these data in very many instances have been published without the detail necessary to that purpose. A decision might have no weight unless it either formulate custom or presage the value of the final standard. Custom is now less easily formulated than when the second edition was written and, insofar as we may judge by past experience in this matter, the acceptance of the "latest value" is a dangerous procedure. However, it is quite impracticable to review all the various standards in detail and some decision must be made for the purposes of this book. I dislike to be merely conservative but am constrained to adhere to the principle stated in the second edition, where it was said: " . . . . it will be wise during the present period of transition to adopt a provisional standard and in lieu of agreement reached in convention to let that standard be in harmony with that tacitly implied in the greater body of data." In one respect the future can be safely predicted. The Bjerrum extrapolation will be abandoned as contributing nothing definite. If so the saturated KCl calomel half-cell will doubtless become the "working standard" and the 3.5 N KCl calomel half-cell will become an "extra" in the scheme. However, while there remains doubt concerning the reproducibility of the saturated KCl calomel half-cell (a doubt which may not be well founded) either the redefined tenth normal calomel half-cell, or the hydrogen half-cell with 0.1 N HCl, will be preferred as the ultimate, practical standard. Of these two half-cells the last has a dangerously high liquid junction potential at the junction HCl | KCl (sat.). Undoubtedly the individual operator will be able to reproduce his data; but the practice has shown such a variety in the manner of forming the liquid junction that the specification of this half-cell would have to involve very careful specification of the manner of forming the liquid junction. Therefore the first half-cell is, for the present, to be preferred.

As already noted, it is impracticable to attempt correction of all[6] important data to strict conformity with the specifications to follow and a certain speciousness results if it be thought that these specifications lead to strict harmony between measurements made accordingly and the

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[6] The data for the buffer mixtures of Clark and Lubs (1916) [see page 200] were obtained with the use of a saturated KCl-calomel half-cell which was standardized against a group of tenth normal KCl calomel half-cells. There were also used Bjerrum extrapolations which were very large in the case of the HCl-KCl mixtures. To conform to the specifications of this chapter the original data have been used in recalculations which are embodied in table 35, page 200.

measurements of the past which were "based on the Sørensen value for the tenth normal calomel half-cell." Nevertheless the agreement should be substantial. That is the best that can be made of the situation.

That a considerable part of the discrepancies appearing in the literature is due to disagreement of primary experimental data rather than to the selection of different bases of reference appears in the footnote to table A, page 672. In that footnote are a few data which, for the most part, represent *direct* measurements. They are compared with the numbers derived from the table. In some instances, such as Walpole's use of a seasoned, saturated, calomel half-cell, and the author's measurement of cell III:VI, the experiments cited are of intermediate measurements and as such are not fundamental. In other instances a careful scrutiny of conditions might reveal reasons for rejecting one or another of the numbers given. However, a comparison of numerous other data, which are less easily compared and tabulated, supports the impression made by this set of comparisons. The problem appears to be quite as much one of technique as of formulation. For this reason recurring shifts of standard and the absence of data revealing the reproducibility of measurements, both of which characterize a considerable part of the modern literature, have made the second decimal of pH numbers as uncertain as they were in a less sophisticated period.

The following specifications are substantially those recommended in the second edition, accepted by Sørensen and Linderstrøm-Lang and then, by a curious fate,[7] abandoned by the latter.

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[7] Originally pH was defined by $pH = \log \dfrac{1}{[H^+]}$. Actually, the numerical values called pH have been determined by dividing the potential of a hydrogen cell by $\dfrac{2.3026 \ RT}{F}$. In the comparison of one solution with a standard solution of hydrion activity of unity, the rigid relation may be written

$$\log \frac{1}{(H^+)} = \frac{-EF}{2.3026 \ RT}$$

where (H^+) represents the hydrogen ion activity of the solution under investigation. Consequently the measured values called pH are $\log \dfrac{1}{(H^+)}$ and not, as defined, $\log \dfrac{1}{[H^+]}$.

Recognizing this Sørensen and Linderstrøm-Lang (1924) proposed that pH retain its original defined meaning and that a new symbol pa_H be used for $\log \dfrac{1}{(H^+)}$.

1. The following half-cell shall be used as a standard of reference

KCl (saturated) | KCl (0.1 N), HgCl(s) | Hg

2. It shall be assumed, arbitrarily, that in the cell

Pt, H$_2$ (1 atmos.) | H$^+$ (activity, X) | KCl (sat.) | KCl (0.1N), HgCl(s) | Hg

　　　　　A　　　　　　　　B　　　　　C　　　　　　　　　D

the potential difference at B remains constant as X varies and that the sum of the potential differences at B, C and D is as follows at each indicated temperature.

Temperature, °C.....	18°	20°	25°	30°	35°	38°	40°
Potential Difference...	0.3380	0.3379	0.3376	0.3371	0.3365	0.3361	0.3358

3. The standard experimental meaning of pH shall be the potential of the above cell considered as of positive numerical

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This proposal is in itself quite consistent and elegant. It provides consistent symbols to be used whenever there is occasion to abbreviate log $\frac{1}{[H^+]}$ and log $\frac{1}{(H^+)}$ in the writing of equations.

But Sørensen and Linderstrøm-Lang went beyond questions of definition and coupled their symbols with two proposed values of the 0.1 N calomel half-cell. One, e.g., 0.3380 at 18°, was to be used in estimating values of pH, and the other, 0.3357, was to be used in calculating values of pa$_H$. Such coupling of the proposals is a source of confusion. Sørensen and Linderstrøm-Lang should have warned their readers that there is no constant difference between hydrogen ion concentration and hydrogen ion activity as implied on page 37 of their article. They appeared to be in agreement with the proposals of the second edition of this book but ignored its proposal of an experimental meaning for a pH *number*.

In their later articles (see, for instance, Sørensen and Linderstrøm-Lang (1927)) they use 0.3357 instead of the older value, 0.3380, for the "0.1 N calomel half-cell."

In this book pa$_H$ is not used. It must be assumed that the reader appreciates the qualifications stated or implied in the use of the laws of an ideal solution. These idealized relations are useful within limits to outline the subject. Then "pH" can retain its original meaning. With regard to meticulous uses the following may be said. Any numerical value given to (H$^+$) implies customary usage. Unless liquid junction potentials are accurately estimated when the potential of the customary cell is used

value, less the above value for the calomel half-cell pertaining to the temperature used, the difference being divided by the numerical quantity 0.000,198,322 T, where T is the absolute temperature.

4. When a value of pH is modified by attempts to correct for the potentials at B and C, or by the use of some estimated value of the potential at D alone, or by any other modification of the above procedure, a statement of all essential modifications shall be made.

5. If there be used any secondary standard, such as the poten-

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to calculate $\log \dfrac{1}{(H^+)}$, it is not strictly proper to name the calculated value $\log \dfrac{1}{(H^+)}$, or pa_H. However, it is legitimate to proceed with the recognition that the measurement is of an energy relation which if it could be carefully analyzed would give a measure of activity, and to assume *for purposes of approximation* that numbers called "pH" can be used where $\log \dfrac{1}{(H^+)}$ would occur in the energy equation. That the ideal equation in terms of concentrations could not be applied *strictly* has long been recognized, although not emphasized in the past. The modern developments have served to make the emphasis strong but have created no essentially new situation. Since almost all of the values entering our subject are based on the conduct of hydrogen cells they might be renamed pa_H, were the uncertainties of liquid junction potentials adequately taken care of. But, in the absence of finality both in regard to liquid junction potentials and the hydrion activity of any given standard solution, it seems preferable to give an arbitrary but definite meaning to numbers called pH.

That the introduction of pa_H may accomplish no good purpose appears in such comparisons as the following. Hastings, Murray and Sendroy (1927), in using pa_H, with stated assumptions in regard to the calculation of numerical values, find occasion to note that their values differ from similarly named values given by Sørensen and Linderstrøm-Lang. The latter authors in the same year were using 0.3357 for the calomel half-cell while Hastings, Murray and Sendroy were using as a basis of reference $pa_H = 1.08$ for 0.1 N HCl. Both were neglecting the liquid junction between saturated KCl solution and the several solutions placed on the other side of the junction. In the absence of finality in regard to several of the questions concerned it is probable that each set of workers could establish a reasonable justification for the usage they adopted. In that case, and others of like nature, we have different meanings for pa_H so far as its quantitative aspect is concerned.

tial, of a hydrogen electrode or of a quinhydrone electrode in a standard buffer solution, the attempt shall be made to use this standard in accordance with the specifications made above.

It may be emphasized that section 5 provides for the use of any secondary standard if there is no desire to actually use the tenth normal calomel half-cell; but that, if the other specifications are adopted, the secondary standard should not be evaluated *de novo*.

In case the above system is not accepted, it is recommended that every assumption and every detail of the system adopted be carefully stated. In particular it may be said that a statement regarding the potential of a half-cell without statement of assumptions regarding the liquid junctions used in actual cells is misleading.

In the next chapter there will be stated secondary standards which conform more or less closely to the above specifications. Lest the values there stated appear too neglectful of values given elsewhere in the literature let it be said here that the matter has now come to such a pass that it would be impracticable to review and reconcile all the schemes in use.

Experimental and theoretical difficulties with liquid junction potentials are largely responsible for discrepancies in primary experimental data and for diversity of treatment. The cells with which we are chiefly concerned are distinctly different from cells without liquid junction. While the treatment of the latter has been acquiring elegance, demands upon the practical application of the former have left several matters undecided. Indeed it appears as if progress with cells having no liquid junction has created the erroneous impression that our main problem is nearing complete solution. Yet, for the purpose at hand, there is neither adequate knowledge of liquid junction potentials nor adequate information upon the reproducibility and the temperature coefficients of standard half-cells. Therefore that otherwise detestable practice of *arbitrary* standardization seems necessary for the purposes of routine reports.

CHAPTER XXIV

STANDARD SOLUTIONS FOR THE ROUTINE CHECKING OF HYDROGEN ELECTRODE MEASUREMENTS

Thou shalt not have in thy bag divers weights, a great and a small.
Thou shalt not have in thy house divers measures, a great and a small.
But thou shalt have a perfect and just weight, a perfect and just measure shalt thou have.—Deuteronomy, XXV: 13–15.

In the routine measurement of hydrogen ion concentrations it is desirable to frequently check the system. To do so in detail is a matter of considerable trouble; but if a measurement be taken upon some solution of well defined pH, and it is found that the potential of the cell agrees with that which someone has determined by careful and detailed measurements upon all parts, it is reasonably certain that the several sources of E.M.F. are correct.

Any one of the buffer mixtures whose pH value has been established may be used for this purpose, but there are sometimes good reasons for making a particular choice.

In view of the fact that different authors have recently been selecting several reference values which do not agree, there is need that each author state definitely the value selected and the mode of its application. The following discussion concerns values in substantial harmony with the recommendations of the previous chapter,—a restriction made necessary by the fact that discussion of all standards would be impracticable.

STANDARD ACETATE

Michaelis (1914) recommends what has come to be known as "standard acetate." This is a solution tenth molecular with respect to both sodium acetate and acetic acid. Its preparation and hydrogen electrode potential at 18°C. have been carefully

studied by Walpole (1914).   Walpole proposes two methods for its preparation:

(1) From N-sodium hydroxid solution free from carbon dioxid and N-acetic acid adjusted by suitable titration (using phenolphthalein), so as to be exactly equivalent to it.

(2) From N-sodium acetate and N-acetic acid adjusted by titration of a baryta solution, the strength of which is known exactly in terms of the N-hydrochloric acid solution used to standardize electrometrically the normal solution of sodium acetate.

Walpole defines N-sodium acetate as a "solution of pure sodium acetate of such concentration that when 20 cc. are taken, mixed with 20 cc. of N-hydrochloric acid, and diluted to 100 cc., the potential of a hydrogen electrode in equilibrium with it is the same as that of a hydrogen electrode in equilibrium with a solution 0.2 normal with respect to both acetic acid and sodium chloride."   By mixing the N-acetate with the N-HCl in accordance with this definition and then determining the potential of a hydrogen electrode in equilibrium with it, Walpole shows that the N-sodium acetate solution may be accurately standardized.   In table 62 are given Walpole's values showing the relation of the E.M.F. of the chain:

$$- \text{Pt, } H_2 \mid \text{Acetate} \mid \text{KCl (sat.)} \mid \text{KCl (0.1 M) } Hg_2Cl_2 \mid \text{Hg } +$$
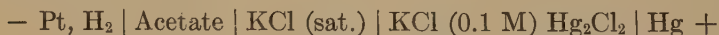
at 18°, to the cubic centimeters of N-HCl added to 20 cc. N-sodium acetate and diluted to 100 cc.   If, for instance, the potential found is 0.4800 volts, the ratio $\dfrac{\text{Concentration of HCl}}{\text{Concentration of NaAc}}$ is $\dfrac{20.2}{20.0}$.   Hence the sodium acetate is 0.9901N.

TABLE 62

CUBIC CENTIMETERS OF N/1 HCl TO 20 CUBIC CENTIMETERS N/1 NaAc DILUTED TO 100 CUBIC CENTIMETERS	E. M. F.
19.00	0.5270
19.40	0.5155
19.50	0.5125
19.90	0.4945
20.00	0.4898
20.39	0.4712
20.89	0.4549
21.00	0.4525

These values are more convenient to use if plotted as Walpole has done.

Walpole found the above cell with "standard acetate" at 18°C. to be 0.6046. The contact potential still to be eliminated was estimated by the Bjerrum extrapolation to be 0.0001 volt. This is negligible.

The value 0.6046 seems to be the value of the chain corrected to one atmosphere hydrogen plus vapor pressure.

$$\frac{M}{20}\text{ ACID POTASSIUM PHTHALATE}$$
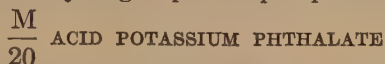
It will be noted that both Sørensen's standard glycocoll (see page 486) and the standard acetate solutions must be constructed by adjustment of the ratio of the components. While there is no great difficulty in this there remain the labor and the chance of error that are involved. Clark and Lubs (1916) have shown that acid potassium phthalate possesses a unique combination of qualities desirable for the standard under discussion. The first and second dissociation constants of phthalic acid are so close to one another that the second hydrogen comes into play before the first is completely neutralized (see fig. 5 page 28). As a consequence the half-neutralized phthalic acid (KH Phthalate) exhibits a good buffer action. The salt of this composition crystallizes beautifully without water of crystallization, and, as was shown by Dodge (1915) and confirmed by Hendrixson (1915) it is an excellent substance for the standardization of alkali solutions. As such it is used to standardize the alkali entering into the buffer mixtures of Clark and Lubs (see page 197). The outstanding feature is that the ratio of acid to base is fixed by the composition of the crystals and not by adjustment as in other standards. The salt may be dried at 105°C. and a solution of accurate concentration constructed.

The original data of Clark and Lubs (1916) for the cell

Pt, H_2 (1 atmos.) | KH Phthalate (0.05 Molar) | KCl (sat.)
                                                    B
                  | KCl (0.1 N), HgCl | Hg
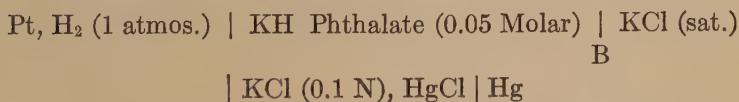
was 0.5689 volts at 20°C. Using 0.3379 for the half-cell to the right of B and neglecting liquid junction potential at B, we obtain pH = 3.974.

If we assume inappreciable change in this value between 18°
and 40° [see Kolthoff and Tekelenburg (1927)] we obtain the
following tentative values.

Half Cell I: Pt, H_2 (1 atmos.) │ KH Phthalate │ KCl (sat.)‖
                                      │ 0.05 M   │

Cell II: Half cell I │ KCl (sat.) │ KCl (0.1 N), HgCl │ Hg
Cell III: Half cell I │ KCl (sat.), HgCl │ Hg
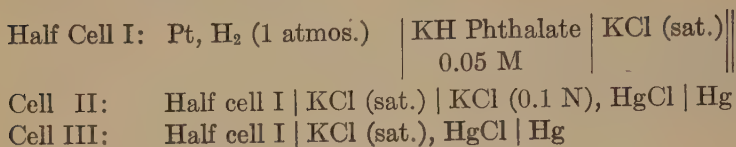
TABLE 63

TEMPERATURE	POTENTIAL IN VOLTS OF CELL OR HALF-CELL		
	I	II	III
°C.	volts	volts	volts (approx.)
18	−0.2292	0.5672	0.480
20	−0.2310	0.5689	0.481
25	−0.2347	0.5723	0.481
30	−0.2386	0.5757	0.481
35	−0.2426	0.5791	0.481
38	−0.2449	0.5810	0.481
40	−0.2465	0.5823	0.481

There have been objections to the use of phthalate solutions
as standards, based upon the reduction of phthalate at the hydro-
gen electrode.   A discussion of this is found on page 437.   See
also Kolthoff and Tekelenburg (1927).

OTHER STANDARD BUFFERS

Any one of the buffer mixtures having a well defined pH-value
may be used.   There then is implied the acceptance of the
standard conditions under which the pH value was determined
in the first instance.   Sørensen (1909), having established his
basis by the method indicated in the previous chapter, used that
mixture of eight volumes of his standard glycocoll to two volumes
of his standard hydrochloric acid which is described in Chapter IX.

HYDROCHLORIC ACID SOLUTIONS

Sørensen and Linderstrøm-Lang (1924), Cullen, Keeler and
Robinson (1925), Michaelis, Kolthoff and others advocate

0.01 N HCl + 0.09 N KCl, or other mixtures of low acid concentration. See Michaelis and Kakinuma (1923), Michaelis and Fujita (1923) and Michaelis and Mizutani (1924), Biilmann (1927) and page 472. Michaelis and Krüger (1921) use 0.0025 N HCl + 0.0975 N KCl. Because of the difficulty of calculating (H^+) in such mixtures 0.1 N HCl is preferred by some.

In the use of 0.1 M HCl solution as a working standard the inclination has been to make it the ultimate standard. However, attention has been called to the fact that the liquid junction potential is a difficult matter to handle both experimentally and theoretically. It is doubtful whether these standards are well adapted to routine standardization.

With this caution we may call attention to the pH values stated in table 35a, page 201, and to the corresponding hydrogen electrode potentials given in table A, page 672.

"TENTH NORMAL CALOMEL HALF-CELL"

For convenience we shall repeat here the arbitrarily assigned values of the practical half-cell

| KCl (sat.) | KCl (0.1 N) HgCl | Hg
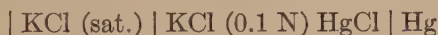
This is not the half-cell

|| KCl (0.1 N), HgCl | Hg

which is the true tenth normal calomel half-cell without liquid junction.

TABLE 64

Arbitrary values of practical tenth normal calomel half-cell

t	POTENTIAL	t	POTENTIAL
°C.		°C.	
18	0.3380	35	0.3365
20	0.3379	38	0.3361
25	0.3376	40	0.3358
30	0.3371		

SATURATED KCl CALOMEL HALF-CELL

As stated in Chapter XXII the temperature coefficient is uncertain. The values given in Chapter XXII are as shown in table 65.

TABLE 65

t	POTENTIAL	t	POTENTIAL
°C.		°C.	
18	0.251	35	0.238
20	0.250	38	0.236
25	0.2458 ·	40	0.234
30	0.242		

QUINHYDRONE HALF-CELLS

See Chapter XIX.

CAUTION

The investigator who has been following a particular system of standardization may find in table A, page 672, one or another value which he is prepared to dispute. The author's own data for the "saturated calomel half-cell" at 30°C. is appreciably higher than that given in the table. Attention has been called to the unsatisfactory temperature coefficient in this case. See page 455. At several points in this book attention is being called to several matters which need investigation. Emphasis of this aspect seems wiser than partiality in the selection of values. The emphasis seems particularly important at the present time because in some instances the elegancies of formulation have obscured discrepancies in experimental data.

In addition the assumption on which table A is based introduces a source of discrepancy.
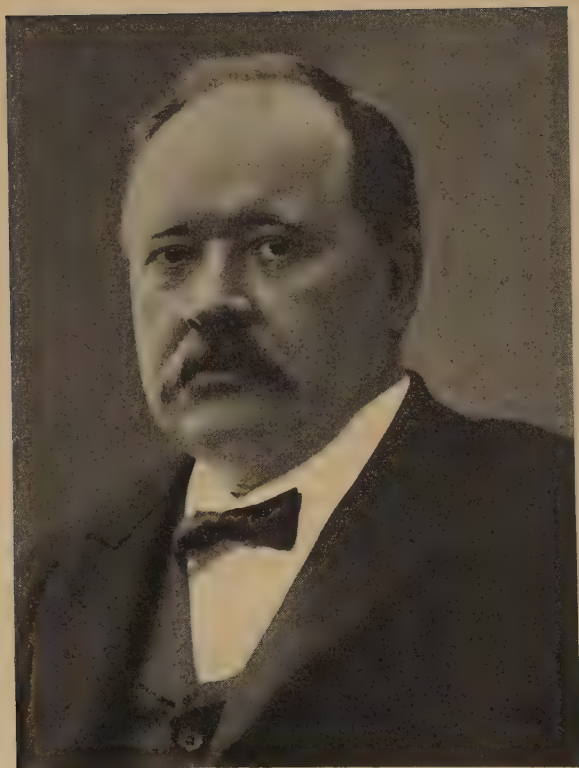
Svante Arrhenius.

CHAPTER XXV

THE THEORY OF DEBYE AND HÜCKEL

I am not satisfied with the view so often expressed that the sole aim of scientific theory is "economy of thought." I cannot reject the hope that theory is by slow stages leading us nearer to the truth of things.—A. S. EDDINGTON.

INTRODUCTION

The chemist who is untrained in the methods of mathematical physics will regard the papers of Debye and Hückel as of "frightful mien;" but he is becoming familiar with the simple, final equations as they occur with ever increasing frequency in current journal articles, and as they are applied to a wide variety of important problems. The theory attains its momentum at the time our respected and beloved Arrhenius passes from the world. It will doubtless come to be regarded as the greatest of the justifications of Arrhenius' brilliant theory. This is not alone because it deals vigorously with those anomalies which have constituted the weak point in the theory of electrolytes; it is largely because Debye and Hückel, going in the direction indicated by Milner, have established connection between the more purely thermodynamic trend of the recent period and statistical mechanics. This achievement, and the fact that it is stimulating new types of investigation, mark the beginning of a new period in the development of Arrhenius' theory. The achievement is injured but little by the several stated and implied limitations imposed by the introduction of simplifying assumptions in the first struggle with the difficulties.

Because of the difficult mathematical argument used by Debye and Hückel, I cannot discuss the details. Only the outline will be given. No doubt this will not be considered satisfactory by those who are well acquainted with the subject. However, the importance of the theory is my justification for an attempt to sketch the argument. If a reader will not make the mistake of using such an outline when he should consult the original papers

he may find it to be of some aid to his understanding of what the simple final equations are *about*.

The central idea in the theory of Debye and Hückel (1923) is this: Although ions in solution may not obey strictly the ideal gas laws because of the same sort of interferences which obtain in the case of neutral molecules, there is, in the case of ions, the added interference of the mutual interaction of the electrically charged particles. Account of this must be taken when there is formulated the free energy of transfer of a particular kind of ion from one concentration to another, because the free energies of separation at two different ion concentrations differ. Dilution of a solution increases the dispersion with consequent closer approach of the conduct of the ions to the laws of the ideal gas. Were this interionic action *alone* responsible for deviations from the gas laws, its effect should fully account for those correction terms which we have previously described as the activity coefficients. (See Chapter XI, page 236.) Debye and Hückel show that on this basis the correction terms for *very dilute* solutions can be calculated.

One of the most important of the main results is the following simple equation, applicable to *very* dilute aqueous solutions at 25°C.

$$- \log \gamma_i = 0.5 \, z_i^2 \, \sqrt{\mu}$$

where γ_i is the activity coefficient of an ion of the ith kind with valence z_i, and where μ is the "ionic strength" of the solution. The ionic strength of the solution is obtained by multiplying the concentration of each ion by the square of that ion's valence number, summing all these products and dividing the result by two.

The equation written above is a limiting equation applicable only at very high dilution. For moderately dilute solutions the average diameter of the ions is taken into account and the equation then is

$$- \log \gamma_i = \frac{0.5 \, z_i^2 \, \sqrt{\mu}}{1 + 3.3 \times 10^7 \, a \, \sqrt{\mu}}$$

where **a** is the average ionic diameter.

DERIVATIONS

Fix attention upon a positive ion (see figure 85). Let it have an effective radius **a**, by which will be understood a limit within which other ions cannot penetrate. This radius, **a**, will enter the argument later. Concentric with the ion considered, imagine there to be shell of radius r, in which we find an element of space of infinitesimal thickness dr and infinitesimal volume dv, situated as shown in figure 85.

The first problem is to find some expression for the relative numbers of positive and negative ions which will enter dv, which is in the electric field of the central ion.

For this purpose there is used the Boltzmann principle. We shall employ it somewhat loosely.
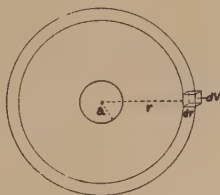
FIG. 85

When a positive ion enters dv it gains potential energy of position by reason of its approach to the repelling central ion. Likewise when a negative ion enters dv it loses potential energy. When an ion enters dv let ΔF be the gain in energy per mole of a positive ion of valence z_a. Let N_o represent the Avagadro number. Let $[a]_1$ be the concentration of positive ions of the ath kind expressed in moles *per cubic centimeter*.[1] Let ϵ be the elementary electric charge and ψ the potential.

$$[a]_1 \, dv \, \Delta F = (N_o[a]_1 \, dv \, z_a\epsilon)\psi \qquad (1)^2$$

Were there no interionic force, the positive ions of the ath

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[1] This space relationship will later be translated to moles per liter.

[2] $N_o[a]_1 \, dv$ gives the number of particles and $N_o[a]_1 \, dv \, z_a\epsilon$ the number of charges. The number of unit charges multiplied by the potential at the place found is the energy required to bring the ions from a place of zero potential.

kind would be evenly distributed and their concentration would be, stoichiometrically, $[a]_2$. Except for the work included in ΔF we will assume that the ions behave as an ideal solute. Then the free energy of transfer between an imagined homogenous solution in which the concentration is $[a]_2$ and the place where the concentration is $[a]_1$ is given by (2).

$$- \Delta F = \text{RT } ln \frac{[a]_1}{[a]_2} \tag{2}$$

Apply (2) to account for the energy-change *locally* between the condensed state and that of complete dispersion. A combination of equations (1) and (2) gives (3)[3] where e is the base of Naperian logarithms.

$$[a]_1 = [a]_2 \left(e - \frac{N_o^- \, z_a \, \epsilon \, \psi}{\text{RT}} \right) \tag{3}$$

This is a special application of the Boltzmann principle.[4] Equation (3) states that the concentration of the ions in dv, namely $[a]_1$ is a function first of the concentration, $[a]_2$, which would be found there were there no interionic force and second an exponential function of the ratio of the potential energy to the thermal energy. The parenthesized term of (3) can be expanded by the formula

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} \quad \text{etc.}$$

(See Mellor, *Higher Mathematics*.) An approximation[5] is here

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[3] $x = y \, ln \, w$ may be written $w = e^{\frac{x}{y}}$. Hence $\frac{[a]_1}{[a]_2} = e^{\frac{-\Delta F}{\text{RT}}}$.

[4] See p. 1025 of article by Dushman in Taylor's *Treatise on Physical Chemistry*.

[5] Instead of the approximation being presented in this way, it is sometimes found that the equations are kept in exponential form till the equation for the density δ, appearing in our equation (6), is in exponential form. Then there appears the term

$$e^{-\frac{\epsilon\psi}{\text{RT}}} - e^{+\frac{\epsilon\psi}{\text{RT}}}$$

which is $-2 \sin \text{hyp} \frac{\epsilon\psi}{\text{RT}}$. Here "sin hyp," sometimes written "sinh," signifies *hyperbolic sine* (see Mellor-Higher Mathematics). It is at this point that the approximation is introduced since $-2 \sin \text{hyp} \frac{\epsilon\psi}{\text{RT}}$ is approximately $-2 \frac{\epsilon\psi}{\text{RT}}$.

considered permissible and all terms after the second are ignored. Then (3) becomes:

$$[a]_1 = [a]_2 - [a]_2 \frac{N_o\, z_a\, \epsilon\, \psi}{RT} \qquad (4)$$

Likewise for a negative ion of the bth kind and valence z_b:

$$[b]_1 = [b]_2 + [b]_2 \frac{N_o\, z_b\, \epsilon\, \psi}{RT} \qquad (5)$$

Confine attention for the moment to a solution which contains only ions of the kinds a and b. The density of electrostatic charge in any element of volume dv is determined by the difference between the numbers of positive and negative charges brought there by these ions. If this density be denoted by δ,

$$\delta = N_o\, [a]_1\, z_a\, \epsilon - N_o\, [b]_1\, z_b\, \epsilon \qquad (6)$$

Combination of (4), (5) and (6) yields (7).

$$\delta = (N_o\, [a]_2\, z_a\, \epsilon - N_o\, [b]_2\, z_b\, \epsilon) - \frac{N_o^2\, \epsilon^2\, \psi}{RT} \left[[a]_2\, z_a^2 + [b]_2\, z_b^2 \right] \qquad (7)$$

Since the subscripts "2" refer the concentrations to the stoichiometrical, the rule of electroneutrality of the solution *as a whole* demands that the first parenthesized two terms to the right of (7) reduce to zero. Were more than two kinds of ions concerned, there would appear a similar but more extended set of these terms, but the differences between them would be zero. To express the more general equation the bracketed part of the last term in (7) may be replaced by Σ (cz^2) which indicates that the concentration per cubic centimeter of each ion is to be multiplied by the square of that ion's valence and all such products added together. Equation (7) may then be written in the more general form of (8)

$$\delta = - \frac{N_o^2\, \epsilon^2\, \psi}{RT} \Sigma\, (cz^2) \qquad (8)$$

There is now to be found a relation between the density of electrostatic charge, δ, the potential ψ and the radial distance, r,

of the element of volume dv from the central, positive ion.   Here there is applied Poisson's[6] equation, which is:

$$\frac{1}{\mathrm{r}^2}\frac{d}{d\mathrm{r}}\left(\mathrm{r}^2\frac{d\psi}{d\mathrm{r}}\right) = \frac{-4\,\pi\,\delta}{\mathrm{D}} \tag{9}$$

Here D is the dielectric constant of the medium and π has its ordinary mathematical significance.

Substitute (8) in (9) to obtain (10).

$$\frac{1}{\mathrm{r}^2}\frac{d}{d\mathrm{r}}\left(\mathrm{r}^2\frac{d\psi}{d\mathrm{r}}\right) = +\left(\frac{4\,\pi\,\mathrm{N_o^2}\,\epsilon^2\,\Sigma\,(cz^2)}{\mathrm{DRT}}\right)\psi \tag{10}$$

On examination of the coefficient of ψ in (10), it is found to have the dimensions[7] of the square of a reciprocal length.   Designate this length by $\frac{1}{\kappa}$.   Then

$$\frac{1}{\mathrm{l}^2} = \kappa^2 = \frac{4\,\pi\,\mathrm{N_o^2}\,\epsilon^2\,\Sigma\,(cz^2)}{\mathrm{DRT}} \tag{11}$$

[6] It has been said that the introduction of the Poisson equation in the treatment of this subject was a stroke of genius.   By its use Debye and Hückel avoided the chief difficulty encountered by Milner (1912–13) who had mastered the principles of the subject but who failed to develop equations which do not require elaborate trial calculations.

This equation of Poisson (Simeon Denis Poisson, 1781–1840) is

$$\nabla^2\psi = \frac{-4\pi\delta}{\mathrm{D}} \quad \text{Vector Analysis}$$

$$\frac{\partial^2\psi}{\partial\mathrm{x}^2} + \frac{\partial^2\psi}{\partial\mathrm{y}^2} + \frac{\partial^2\psi}{\partial\mathrm{z}^2} = -\frac{4\pi\delta}{\mathrm{D}} \quad \text{Rectangular coördinates}$$

$$\frac{1}{\mathrm{r}^2}\left[\frac{\partial}{\partial\mathrm{r}}\left(\mathrm{r}^2\frac{\partial\psi}{\partial\mathrm{r}}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi}\right]$$

$$= -\frac{4\pi\delta}{\mathrm{D}} \quad \text{Polar (spherical) coördinates}$$

The last equation becomes (9) on the assumption of spherical symmetry. In the equation written in the terms of Vector analysis $\nabla^2\psi$ represents the operation of the next equation. ∇ is called "nabla," "alted" or "del."

For the development of Poisson's equation see Gibbs and Wilson (1925), *Vector Analysis*, pp. 206 and 230.

[7] For brief discussions of dimensions see *Smithsonian Physical Tables* or *International Critical Tables*.

$$\frac{[\mathrm{N_o^2}]\,[\epsilon^2]\,[c]}{[\mathrm{D}]\,[\mathrm{R}]\,[\mathrm{T}]} \equiv \frac{[\mathrm{m^{-2}}]\,[\epsilon^2]\,[\mathrm{ml^{-3}}]}{[\epsilon^2\,\mathrm{f^{-1}}\,\mathrm{l^{-2}}]\,[\mathrm{flm^{-1}}\,\mathrm{T^{-1}}]\,[\mathrm{T}]} \equiv \frac{1}{\mathrm{l}^2}$$

On examining the equations leading to (11) Debye and Hückel find that the length $\frac{1}{\kappa}$ is (approximately) that radial distance at which the density of the ion-atmosphere about the central ion declines an $\frac{1}{e}$ th part.[8]   As shown by (11) this length is determined by the concentrations of the ions, the ion valencies, the dielectric constant of the medium and the temperature.   If, for instance, the temperature T increases, the length increases,—an expression of the tendency of increased thermal agitation to make the ion-distribution more nearly uniform.   If z, any ion valence, increases, the length decreases,—an expression of the local clustering effect of ions with high valence.

Now substitute (11) in (10) and obtain (12), or (12a) (the latter by the notation of footnote 6).

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \kappa^2 \psi \tag{12}$$

$$\nabla^2 \psi = \kappa^2 \psi \tag{12a}$$

Equation (12), or (12a), is a linear differential equation of the second order when all terms involving powers of ψ greater than one are suppressed in accordance with the first approximation noted on page 492.   Then the solution of (12) becomes:

$$\psi = A \frac{e^{-\kappa r}}{r} + A' \frac{e^{\kappa r}}{r} \tag{13}[9]$$

[8] The conception involved is of importance to the treatment of the so-called Helmholtz double-layer.   Consider a particle or an electrode surface which, for any reason, has a potential different from the solution with which it is in contact.   There will be near the interface a greater density of positive or negative ions according to the sign of the relative potential of the particle or electrode.   The distance $\frac{1}{\kappa}$ represents the distance at which the potential difference has declined to $\frac{1}{e}$ th of its value at the interface considered as a mathematical surface.

For a discussion of the applicability of this concept to the study of the precipitation of colloids by neutral salts see Burton (1926) and forthcoming article by Mueller.

[9] The general solution of (12) has been given by Gronwall (1927).   A more complete treatment is to appear in Physik. Zeit. in a joint paper with LaMer and Sandred.—Personal correspondence with Dr. V. K. LaMer.

In equation (13) A and A′ are integration constants. Of these A′ must be zero; otherwise ψ would approach infinity instead of zero as r approaches infinity. Hence

$$\psi = A \frac{e^{-\kappa r}}{r} \tag{14}$$

The linear approximation can be obtained as follows. Perform the indicated operations to obtain the identities:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) \equiv \frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} \equiv \kappa^2 \psi \tag{12}$$

Multiply by r and transpose to obtain:

$$r \frac{d^2\psi}{dr^2} + 2 \frac{d\psi}{dr} - \kappa^2 (r\psi) = 0 \tag{a}$$

or

$$\frac{d^2 (r\psi)}{dr^2} - \kappa^2 (r\psi) = 0 \tag{b}$$

We now have r ψ as variable instead of ψ.
Let

$$r\psi = y \tag{c}$$

Then

$$\frac{d^2 y}{dr^2} - \kappa^2 y = 0 \tag{d}$$

Now try the solution

$$y = e^{\lambda r} \tag{e}$$

Then

$$\frac{d^2 y}{dr^2} = \lambda^2 e^{\lambda r} \tag{f}$$

Hence by (e), (f) and (d)

$$\lambda^2 e^{\lambda r} - \kappa^2 e^{\lambda r} = 0 = e^{\lambda r} (\lambda^2 - \kappa^2)$$

or

$$\lambda = \pm \kappa \tag{g}$$

Now combine (g) and (e)

$$y = e^{\pm \kappa r} \tag{h}$$

Substitute (h) in (c)

$$r\psi = e^{\pm \kappa r}$$

or in general

$$r\psi = Ae^{-\kappa r} + A'e^{\kappa r} \tag{i}$$

where A and A′ are integration constants.

Equation (i) is identical with (13) of the text. The result may be verified by performing the operations indicated by the operator $\nabla^2 \psi$ of equation (12a). See footnote 6.

The potential ψ_i at any point in the interior of the central ion (see figure 85) of valence z_i is:

$$\psi_i = \frac{z_i\,\epsilon}{Dr} + B \qquad (15)^{10}$$

where $\frac{z_i\epsilon}{Dr}$ is the part contributed by the ionic charge of the central ion and B is the part contributed by the surrounding ion-atmosphere. In the description of figure 85 it was specified that a is the limit of approach of other ions to the central ion. *At this limit* the potential of the surrounding ion-atmosphere, given by (14), must equal ψ_i given by (15). Also at this limit r = a. Then

$$A\frac{e^{-a\kappa}}{a} = \frac{z_i\,\epsilon}{Da} + B \qquad (16)$$

Furthermore the field strengths $\frac{d\psi}{da}$ must become equal. Hence differentiate (14) and (15) and equate by $\frac{d\psi}{dr} = \frac{d\psi_i}{dr}$ letting r = a.

$$Ae^{-a\kappa}\left(\frac{1+a\,\kappa}{a^2}\right) = \frac{z_i\,\epsilon}{Da^2} \qquad (17)$$

Solve for A, substitute in (16) and find B.

$$B = -\frac{z_i\,\epsilon\,\kappa}{D(1+\kappa\,a)} \qquad (18)$$

These steps have not only yielded the integration constant, A, of (14) but have led directly to B, the desired quantity, which is the potential of the central ion due to the surrounding ion-atmosphere, assuming that there is a definite limit, a, to the approach of the ion-atmosphere. If the central ion, instead of being the positive ion considered so far, has a valence $\pm z_i$, the work of removal will be:

$$\pm\frac{z_i\,\epsilon\,(\mp B)}{2} = +\frac{z_i^2\,\epsilon^2\,\kappa}{2\,D(1+\kappa\,a)} \qquad (19)$$

[10] This may be derived from Poisson's equation by making $\delta = 0$.

For N_o ions the work, w, of removal will be:

$$w = \frac{N_o\, z_i^2\, \epsilon^2\, \kappa}{2\, D(1 + \kappa\, a)} \qquad (20)$$

In (20) w is the free energy[11] involved in the removal of one mole of ions of the ith kind from the electrical field of their ion-atmospheres to an infinitely dilute solution of the same medium at the same temperature.

If two solutions of these ions of concentrations C_1 and C_0 were ideal, the free-energy of transfer would be

$$-\Delta F = RT\, ln\, \frac{C_1}{C_0} \qquad (21)$$

If the solution of concentration C_1 were not ideal but that of the infinitely dilute solution of concentration C_0 were ideal, the observed free energy increase would be

$$-\Delta F = RT\, ln\, \frac{C_1}{C_0} + RT\, ln\, \gamma_1 \qquad (22)$$

where γ_1 is the activity coefficient described on page 236. On the assumption that the interionic electrostatic forces are alone responsible for deviation from the ideal (or limiting) law of solutions it is obvious that the term $RT\, ln\, \gamma_1$ of (22) is $-w$ of (20), and that, when solutions are being described by the ideal laws, this term must be applied as a correction. Hence

$$-ln\, \gamma_i = \frac{N_o\, z_i^2\, \epsilon^2\, \kappa}{2\, DRT(1 + a\, \kappa)} \qquad (23)$$

The equivalent of κ by equation (11) will now be recalled; but instead of retaining c, moles per cubic centimeter, we shall use C, moles per 1000 cubic centimeters (approximately moles per liter). Then equation (11) becomes (24).

$$\kappa = \sqrt{\frac{4\,\pi\, N_o^2\, \epsilon^2\, \Sigma\, (Cz^2)}{1000\, DRT}} \qquad (24)$$

[11] "Free energy" (Lewis) by reason of the nature of the method of measurement of the electrical quantities involved. See Debye (1925), Bjerrum (1926), Brønsted (1927) and particularly E. Q. Adams (1926).

In combining equations (23) and (24) we may segregate the universal constants, N_o, ϵ, R, and π and may substitute their numerical values.

$$N_o = 6.061 \times 10^{23}; \quad \varsigma = 4.774 \times 10^{-10};$$
$$R = 8.315 \times 10^7; \quad \pi = 3.1416.$$

Equation (23) will also be transformed to the use of logarithms to the base 10.[12] There will then remain two quantities D, the dielectric constant, and T, the absolute temperature, which may be given numerical values only under special conditions. To note how variations of D and T affect the calculated numerical form of the equation it will be convenient to write the combined equations (23) and (24) as follows:

$$- \log \gamma_i = \frac{\mathfrak{A}\, z_i^2\, \sqrt{\Sigma\,(Cz^2)}}{1 + \mathfrak{B}\, a\, \sqrt{\Sigma\,(Cz^2)}} \tag{25}$$

where

$$\mathfrak{A} = \frac{1.2833 \times 10^6}{(DT)^{1.5}} \tag{26}$$

and

$$\mathfrak{B} = \frac{3.557 \times 10^9}{(DT)^{0.5}} \tag{27}$$

In place of $\Sigma\,(Cz^2)$, used in the above, there is usually employed Lewis' μ, which is called the *ionic strength* and defined by:

$$\mu = \frac{1}{2}\,(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 +, \quad \text{etc.}) \tag{28}$$

Here m_1, m_2, m_3 etc., are the molalities (moles per 1000 grams of solvent) of the ions. Since the Debye-Hückel theory was derived with the aid of space relations, concentrations should be expressed in moles per 1000 cc. However, assuming the distinction between moles per 1000 cc., moles per liter and moles per 1000 grams water to be negligible, we may write

$$2\mu = \Sigma\,(Cz^2)$$

[12] By use of: $ln\mathrm{x} = \log_e \mathrm{x} = 2.3026 \log_{10} \mathrm{x} = 2.3026 \log \mathrm{x}.$

Then equation (25) becomes:

$$- \log \gamma_1 = \frac{\mathfrak{A} \sqrt{2} \, z^2 \, \sqrt{\mu}}{1 + \mathfrak{B} \sqrt{2} \, a \, \sqrt{\mu}} \tag{29}$$

For values of $\mathfrak{A}$, $\mathfrak{A}\sqrt{2}$, $\mathfrak{B}$ and $\mathfrak{B}\sqrt{2}$ see table 66.

TABLE 66

Coefficients for the Debye-Hückel equation

$$\mathfrak{A} = \frac{1.2833 \times 10^6}{(DT)^{1.5}} \qquad \mathfrak{B} = \frac{3.557 \times 10^9}{(DT)^{0.5}}$$

t° (CENTI-GRADE)	T	D*	$\mathfrak{A}$	$\mathfrak{B}$	$\mathfrak{A}\sqrt{2}$	$\mathfrak{B}\sqrt{2}$
0	273.1	88.0	0.344	2.29×10^7	0.487	3.24×10^7
15	288.1	82.5	0.350	2.31×10^7	0.495	3.26×10^7
18	291.1	81.0	0.354	2.32×10^7	0.501	3.28×10^7
20	293.1	80.5	0.354	2.32×10^7	0.501	3.28×10^7
25	298.1	78.8	0.356	2.32×10^7	0.504	3.28×10^7
30	303.1	77.0	0.360	2.33×10^7	0.509	3.29×10^7

* The values for the dielectric constant of water as given in the literature vary to an extent important to the present purpose. Since this situation is stimulating reinvestigation of the subject, the reader will look for new values in the literature subsequent to the publication of this book and will realize that the values given above are purposely rounded.

Table 66 shows that temperature has little effect upon the magnitude of the coefficients. Therefore the final equation (29) may be simplified to:

$$- \log \gamma_1 = \frac{0.5 \, z_i^2 \, \sqrt{\mu}}{1 + 3.3 \times 10^7 \, a \, \sqrt{\mu}} \tag{29a}$$

The constant, **a**, was specified to be the radial distance within which other ions could not approach the central ion of figure 85; but, in the course of the development of the final equations, **a** should be reinterpreted as the average effective diameter of all the ions. In the absence of experimental, specific values for this average effective diameter of the possibly hydrated ions, the constant, **a**, becomes more or less an arbitrary constant. To **a** ascribe the value 1×10^{-8}, which is merely the order of magnitude of ion diameters. It is then readily calculated, by equation

(28) and the values of $\mathfrak{B}\sqrt{2}$ in table 66, that, when $\sqrt{\mu}$ is less than the order of magnitude 0.1, equation (29a) reduces practically to:

$$- \log \gamma_i = 0.5 \, z_i^2 \, \sqrt{\mu} \qquad (29b)$$

There are several experimental verifications of this last simple equation (29b) at the high dilution called for by the above condition that $\sqrt{\mu} < 0.1$. Furthermore the introduction of an average diameter, a, of a reasonable order of magnitude *tends* to extend the verification of the Debye-Hückel theory by making (29a) appear applicable to somewhat more concentrated solutions.

The above equations relate to the activity coefficient of an ion of the ith kind. If a salt dissociate so that each molecule furnishes z_a ions of the bth kind and z_b ions of the ath kind, z_a being the valence of the "a" ion and z_b the valence of the "b" ion, the mean activity coefficient of the ions, γ_s, may be defined by

$$\log \gamma_s = \frac{z_b \log \gamma_a + z_a \log \gamma_b}{z_a + z_b} \qquad (30)$$

Application of (29b) then yields (31)

$$- \log \gamma_s = 0.5 \, z_a z_b \, \sqrt{\mu} \qquad (31)$$

If a salt like $MgSO_4$ dissociate to two ions of the same valence number, equation (31) is obtained again for this case.

For salts of different valence-type the coefficient $0.5 \, z_a z_b$ for 25°C. has the values shown below.

EXAMPLE	VALENCE-TYPE	COEFFICIENT
KCl....................................	1–1	0.5
K_2SO_4..................................	1–2	1.0
$Al(NO_3)_3$................................	3–1	1.5
$MgSO_4$...................................	2–2	2.0
$Ca_3(PO_4)_2$..............................	2–3	3.0
$(Co(NH_3)_6)(Co(CN)_6)$...................	3–3	4.5

DISCUSSION

There have been numerous experiments designed to test the simple equation applicable at high dilution where the average

ionic diameter is negligible and also to test the equation containing **a**, the average ionic diameter. These experiments cover variation of dielectric constant by the use of solvents of various dielectric constant; they cover variation of the ionic strength in which the ionic strength is obtained with salts of very different valence-type; they cover measurements of the activity coefficients of solutes of very different valence-types.

See Noyes *et al.* on various tests of the Debye-Hückel equation.

Substantially, the theory in the quantitative form given by the equations is confirmed as a *limiting law;* but obviously the theory makes no pretense to deal with effects other than the electrostatic and there are two approximations introduced. One is the use of the dielectric constant of the solvent in place of the dielectric constant of the solution. Hückel (1925) attempts to correct for this. He introduces a reasonably deduced additional term. The other approximation is in the mathematical development. It is in the step taken to reach equation (4). After expanding the series term only the first two terms of the expansion were considered. LaMer (1927) claims that a consideration of the higher terms is sufficient to account for the major portion of those discrepancies between theory and experiment which have been particularly noticeable with salts of high valence, since

a factor $\dfrac{z^2}{a}$ enters at successively higher powers for each successive approximation in the solution of equation (12). When $\dfrac{z^2}{a}$ is greater than 0.5 (i.e. when **a** is less than two Ångstrom units for a uni-univalent salt, or less than eight Ångstrom units for a bivalent salt) a consideration of the Debye approximation alone gives distorted calculated results and quite misleading values of "a" according to LaMer. When $\dfrac{z^2}{a}$ approaches unity, the influence of the higher terms is sufficient to make it appear as if the limiting slope were larger than its value of 0.5 at concentrations as low as those corresponding to 0.001μ. For further details of this aspect see a forthcoming paper by LaMer, Gronwall and Sandred.[13]

[13] Private correspondence with Dr. LaMer.

There has also been considered the inherent difficulty resulting from the assumption that the ions have spherical fields. This is to neglect, not only the spatial configurations demanded especially of organic molecules, but also the polarities of large ions.

Pending the highly refined investigations, experimental and theoretical, which are expected to throw light upon the manner in which these and other details of the theory are to be handled, we may consider the Debye-Hückel theory from the following two points of view.

In the first place the theory has been so well substantiated in its main outline that we may have considerable confidence in using the reduced equation to calculate corrections of the *first order* for *very dilute* solutions (e.g. $\sqrt{\mu} < 0.1$). For solutions of slightly higher ionic strength it will be recalled that the apparent ionic diameter enters as of numerical significance. That the use of values of a reasonable order of magnitude leads to corrections in the right direction is of general theoretical interest.

In the second place it will be well to remember that there are some conflicting views regarding several aspects of the theory. Mention was made of LaMer's objection to the approximation in the expansion of the series (see page 492). Others believe this objection to be not serious. By adjusting the value of **a** in equation (29) there is extended the range of concentrations within which experimental data conform to the calculated curves. Such adjustment will be considered empirical curve-fitting by some. Others will regard it as entirely justified by the demands of the theory.

It is not the function of this outline to discuss these and several other matters which are now under discussion. The point to be emphasized is this. In the immediate future we may expect an orderly presentation of correction terms stated by means of the equations given above.

In addition to the terms stated there is frequently employed an additional term $K_s\mu$ placed as follows

$$- \log \gamma_1 = \frac{0.5 \, z_i^2 \, \sqrt{\mu}}{1 + 3.3 \times 10^7 \, a \, \sqrt{\mu}} - K_s \, \mu.$$

$K_s\mu$ has been called the "salting out term" and is supposed to operate at high salt concentration.

SOME APPLICATIONS

A few examples of the application of the theory follow.

Consider a salt which will not react chemically with the solvent or with other salts present in the solution. Let the salt chosen have a very low solubility and let it be present in the solid phase so that its activity in solution will be maintained constant while the ionic strength of the solution is changed.

$$(\text{salt})_{\text{ in solution}} = (\text{salt})_{\text{ solid phase}}$$

or
$$[\text{salt}]_1\gamma_1 = [\text{salt}]_2\gamma_2 = [\text{salt}]_3\gamma_3 \text{ etc.}$$
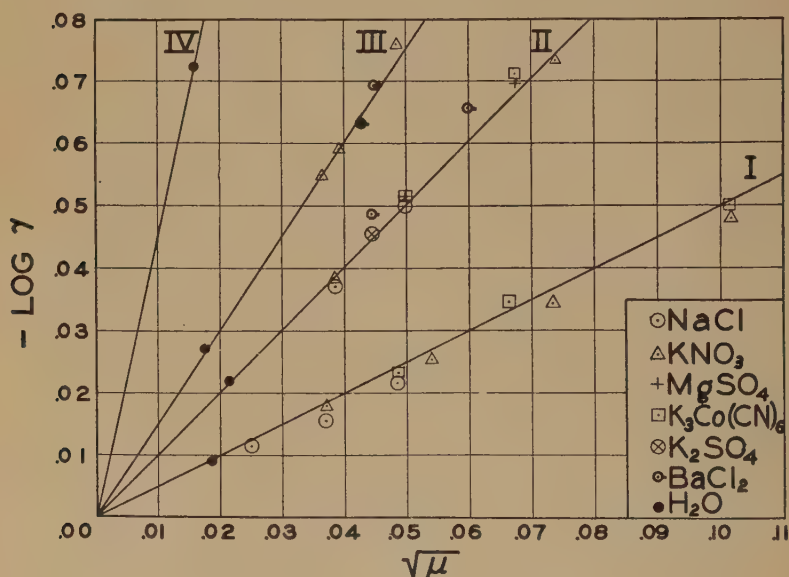
FIG. 86

Here subscripts indicate solutions 1, 2, 3 etc., brackets indicate concentration and parentheses indicate activity. Hence by introduction of equation (31)

$$\log \frac{[\text{salt}]_1}{[\text{salt}]_2} = \log \gamma_2 - \log \gamma_1 = z_a z_b \, 0.5 \left(\sqrt{\mu_1} - \sqrt{\mu_2} \right) \text{ (32)}$$

If a pure, aqueous solution of the salt alone is used, only its ions (and those of water) contribute to μ; but μ may be varied by

adding extraneous salts in various concentrations and various valence-types. These should have effect on the ratio of solubilities $\frac{[salt]_1}{[salt]_2}$ only as they affect μ. On the other hand a change in the valence-type of the salt under study, while still affecting μ, will make itself felt chiefly through new values of $z_a z_b$. For a salt of fixed valence-type the logarithm of the ratio of two solubilities is in linear relation to the increment in the square root of the ionic strength of the solution. At infinite dilution, $\mu = 0$ (neglecting the ions of water) and, since there is no correction to the gas law, $\log \gamma = 0$. Hence the data on solubilities should give a straight line when charted as in figure 86, and this line, extrapolated, should pass through the origin.

In figure 86, reproduced from LaMer's (1927) paper, the curves are for the valence-types tabulated below.

CURVE	SALT	VALENCE-TYPE	SOLUBILITY IN WATER
I	$[Co(NH_3)_4(NO_2)(CNS)]'$ $[Co(NH_3)_2(NO_2)_2(C_2O_4)]'$	1–1	0.000335 M
II	$[Co(NH_3)_4(C_2O_4)]'_2 [S_2O_6]''$	1–2 or 2–1	0.00015 M
III	$[Co(NH_3)_6]''' [Co(NH_3)_2(NO_2)_2(C_2O_4)]'_3$	3–1 or 1–3	0.0000504 M
IV	$[Co(NH_3)_6]''' [Fe(CN_6)]'''$	3–3	0.000030 M

In the figure the salts used to produce variation of μ are indicated.

The extrapolation should lead to the origin $\sqrt{\mu} = 0$ and $-\log \gamma = 0$, i.e., to no correction to the gas laws at infinite dilution.

These data verify the theory. At high dilutions the slope of a curve is that predicted from the numerical form of the equation which takes account of the electrical environment. The valence factor ($z_a z_b$) is correct, since the slopes of the several curves have the corresponding ratios $1:2:3:9$.

While such results are eminently satisfactory, difficulties begin with salts of higher solubilities for the reasons mentioned in the foregoing text. It will be found that a large number of the charts

in the literature take the *form* of one of the curves of figure 87. The linear relation of the reduced equation (31) is seen as a limiting relation obtaining when the ionic diameter approaches zero. The introduction of an assumed ionic diameter (undoubtedly of the right order of magnitude) will give a curve of the form shown in figure 88.

We may now pass to some examples of particular importance to our main subject matter.

Cohn (1927) has gone over the subject of phosphate buffer solutions with the aid of previous data and new data of his own
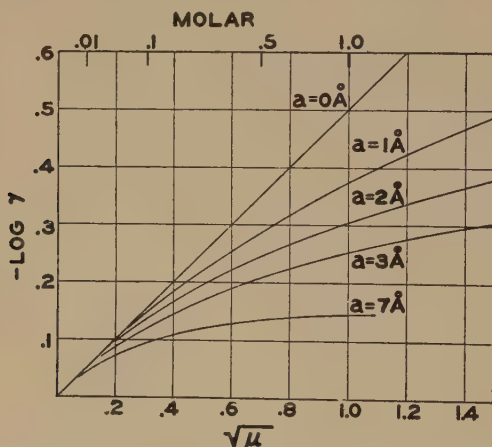
FIG. 87

and has attempted to account for deviations from the simple equilibrium equations by means of the Debye-Hückel equation.

Let us write the relation:

$$\log \frac{1}{(H^+)} = \log \frac{1}{K} + \log \frac{(HPO_4^{--})}{(H_2PO_4^-)} \qquad (33)$$

Here activities are indicated by use of parentheses. Equation (33) can be rewritten as

$$pH = pK + \log \frac{[HPO_4^{--}]}{[H_2PO_4^-]} + \log \frac{\gamma_2}{\gamma_1} \qquad (34)$$

Here brackets represent concentrations.

γ_2 is the activity coefficient of the ion HPO_4^{--}
γ_1 is the activity coefficient of the ion $H_2PO_4^-$

pH is used in (34) in its physical meaning of $\log \dfrac{1}{(H^+)}$, since its values are obtained by the method of the hydrogen electrode.

Assume complete dissociation of salts and therefore that $[HPO_4^{--}]$ and $[H_2PO_4^-]$ are determined from the known concen-
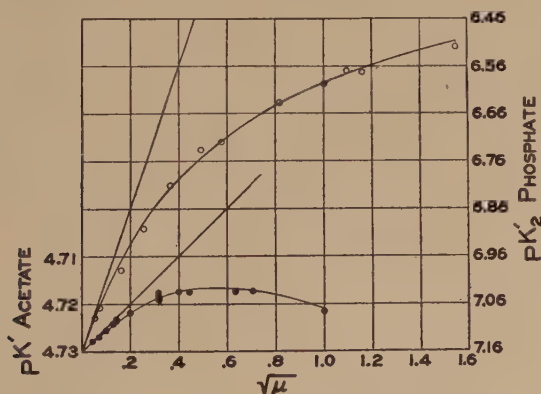
FIG. 88. CORRECTION CURVES FOR pK_2' OF PHOSPHATE ($\bigcirc$) AND pK' OF ACETATE ($\bullet$)

trations of the alkali salts. Now let $\dfrac{[HPO_4^{--}]}{[H_2PO_4^-]} = 1$, and introduce equation (29a) in numerical form.

$$pK = pH - \frac{0.5\sqrt{\mu}}{1 + 3.3 \times 10^7\, a\, \sqrt{\mu}}\, (z_a^2 - z_b^2) \qquad (35)$$

Where z_a is the valence of the ion $H_2PO_4^-$, namely 1; and z_b is the valence of the ion HPO_4^{--}, namely 2. Then (35) is

$$pK = pH + \frac{1.5\sqrt{\mu}}{1 + 3.3 \times 10^7\, a\, \sqrt{\mu}} \qquad (36)$$

If a in (36) were very small the equation would reduce practically to

$$pK = pH + 1.5\sqrt{\mu} \qquad (37)$$

In Chapter I it was shown that under ideal conditions pK = pH when the ratio of concentrations $\dfrac{[HPO_4^{--}]}{[H_2PO_4^-]} = 1$. The term $1.5\sqrt{\mu}$ of the approximate equation (37), or the term $\dfrac{1.5\sqrt{\mu}}{1 + 3.3 \times 10^7\, a\sqrt{\mu}}$ of (36) is then a correction term for the interaction of all the ions present. If the observed values of pH are plotted against the square root of the ionic strength there should be obtained with equation (37) a straight line; and with (36) a set of curves any one of which is dependent on the value of a. In figure 88 the linear relation is shown and also a curve which passes very nicely through or near the observed values. The latter curve is drawn with (36) and Cohn's *assumption* that the mean ionic diameter, a, has the value 5×10^{-8} cm. Although this is a reasonable assumption in so far as it is a possible order of magnitude, it remains an assumption. Yet its use, which in (36) yields (38),

$$pK = pH + \frac{1.5\sqrt{\mu}}{1 + 1.65\sqrt{\mu}} \tag{38}$$

gives a *mathematical* formulation of the observed values which is satisfactory. Another way of showing this is to use (38) as is done in table 67 to calculate pK. It is seen that, whereas the pH values (which should be the constant pK according to the simplified theory of Chapter I) differ in the extreme by 0.568 unit, the corrected values differ in the extreme by only 0.040 unit.

Of course when the ratio of primary to secondary phosphate changes, as it does in ordinary buffer solutions, the value of the ionic strength, μ, changes.

Cohn has also made use of the extended equation:

$$- \log \gamma = \frac{0.5\, z^2\sqrt{\mu}}{1 + 3.3 \times 10^7\, a\sqrt{\mu}} - K_s\mu$$

where $K_s\mu$ is the so-called "salting-out term." K_s varies with the composition of the mixture and is determined empirically. Cohn regards the above formula as an "empirical interpolation formula." With its aid he has prepared a series of charts and tables with which to "facilitate the preparation of buffer solutions

of the same ionic strength and varying pH or the same pH
and varying ionic strength." See page 216.

Cohn, Heyroth and Menkin (1928) have applied the same
principles to acetate systems. This is of particular interest in
connection with the discussion of Chapter I where, with due
warning of the consequences, we found that the application of
the more extended classical equations failed to yield a constant

TABLE 67

Corrected constants for phosphate system (after Cohn, 1927)

EXPERIMENTERS	TOTAL PHOS-PHATE M	IONIC STRENGTH μ	$\sqrt{\mu}$	pH	$\dfrac{1.5\sqrt{\mu}}{1+1.65\sqrt{\mu}}$	pK
	0.00133	0.00267	0.052	7.088	0.071	7.159
	0.00266	0.00532	0.073	7.068	0.098	7.166
Michaelis and Krüger.....	0.00334	0.00667	0.082	7.069	0.108	7.177
	0.01333	0.02667	0.163	6.990	0.193	7.183
	0.03334	0.06667	0.258	6.904	0.272	7.176
Clark and Lubs...........	0.05000	0.10000	0.316	6.843	0.312	7.155
Michaelis and Krüger......	0.06667	0.13333	0.365	6.813	0.342	7.155
Sørensen..................	0.06667	0.13333	0.365	6.813	0.342	7.155
	0.06667	0.13333	0.365	6.817	0.342	7.159
	0.12000	0.2400	0.490	6.737	0.406	7.143
	0.16667	0.3333	0.577	6.721	0.433	7.154
Cohn....................	0.33334	0.6668	0.817	6.638	0.522	7.160
	0.50000	1.0000	1.000	6.599	0.566	7.165
	0.60000	1.2000	1.095	6.570	0.585	7.155
	0.66667	1.33333	1.154	6.573	0.596	7.169
	1.20000	2.4000	1.549	6.520	0.653	7.173
Average..						7.163

$$pK = pH + \frac{1.5\sqrt{\mu}}{1+1.65\sqrt{\mu}}$$

which is satisfactory for other than purposes of approximate
treatment. Cohn, Heyroth and Menkin find that in this case
an apparent error is introduced by use of the value 0.3380 for
the tenth normal calomel half-cell at 18°C. This is because [H⁺]
enters equation (19) of Chapter I in a sum and the higher the
value of the calomel half-cell the higher the apparent value of
[H⁺]. By reducing [H⁺] by use of a smaller value (0.3355) for

the calomel half-cell they find a good correspondence between
calculated and observed corrections. They then find that the
acetate system can be described by

$$\text{pH} - \log \frac{[\text{CH}_3\,\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK} - \frac{0.5\,\sqrt{\mu}}{1 + \text{kb}} + \text{K}_s\,\mu = \text{pK}'$$

The graphically interpolated values for the correction term are
given on page 219. Figure 88 shows the correction for various
dilutions of an equimolecular mixture of acetic acid and sodium
acetate.
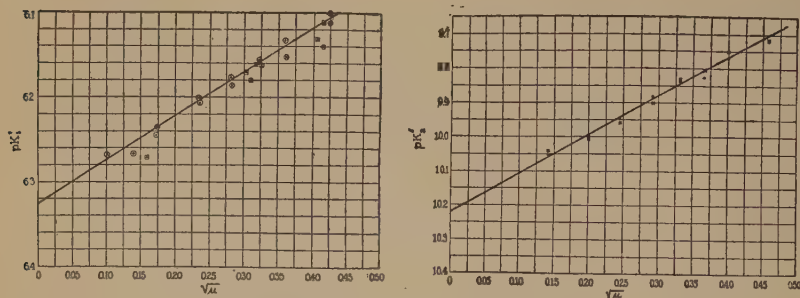
FIG. 89. APPARENT DISSOCIATION EXPONENTS, pK$_1$' AND pK$_2$', OF CARBONIC
ACIDS AT DIFFERENT IONIC STRENGTHS

Left: Points marked ⊙ and ⊗ determined by Hastings and Sendroy;
points marked ⊡ calculated from Warburg's data. Line determined by
pK$_1$' = 6.33 − 0.5 $\sqrt{\mu}$. Right: pK$_2$' = 10.22 − 1.1 $\sqrt{\mu}$. (After Hastings
Sendroy (1925).)

With the phosphate and acetate systems so described it is now
possible to prepare buffer solutions of known ionic strength be-
tween pH 3.6 and 7.6.

Figure 89 shows the effect of ionic strength (plotted as square
root) upon the apparent dissociation constants (in terms of pK')
of carbonic acid as determined by Hastings and Sendroy (1925).

We owe to Brønsted (1921) a first sketch of a possible syste-
matic description of the "salt effects" found in the use of indi-
cators in solutions of different salts. He emphasized the necessity
of introducing the more rigid equations and of considering the
"salt effect" as an expression of the alteration of activity under

specific changes of condition.   v. Halban and Ebert (1924) give
an extensive treatment of picric acid which will repay careful
study.   In this they make use of the Debye-Hückel equation.

I am indebted to Dr. A. B. Hastings and Dr. Julius Sendroy,
Jr., for their permission to publish figure 90 in which they show
the apparent variation of the pK values of indicators as the ionic
strength of the buffer solution is changed by means of different
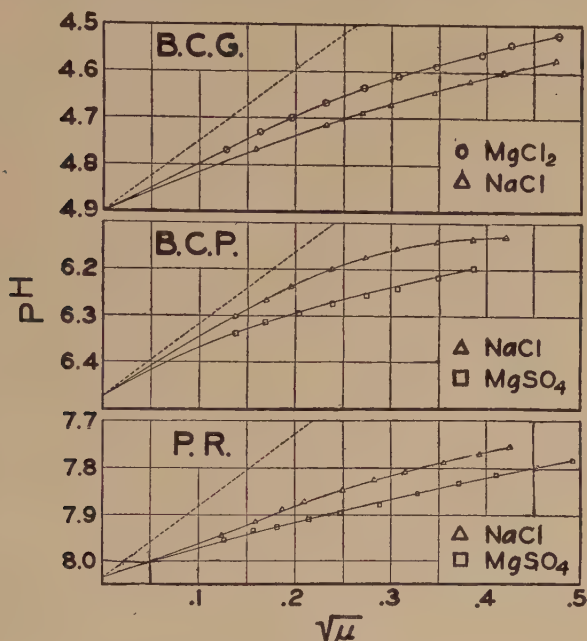
FIG. 90. "SALT EFFECT" WITH INDICATORS
B.C.G. = brom cresol green; B.C.P. = brom cresol purple; P.R. =
phenol red. (Courtesy of Hastings and Sendroy.)

buffers and added salts of various types.   Although the limiting
equation is inapplicable these investigators have systematized the
experimental data in a way which is of far greater value than
the loosely constructed tables of the past, and by use of the
coördinates — log γ and $\sqrt{\mu}$.   There remains distinct evidence
of "specific salt errors."   This shows that, in the use of indicators
with specific solutions, experimental calibration must still be used
whenever precise values are to be stated.

REVIEWS

The Theory of Strong Electrolytes. A general discussion held by The Faraday Society, Trans. Faraday Soc., April, 1927.

LaMer. Recent Advances in the Ionization Theory as Applied to Strong Electrolytes. Trans. Am. Electrochem. Soc., April, 1927.

Scatchard. The Interaction of Electrolytes with Non-electrolytes. Chem. Rev., *3*, 383 (1927).

Annual Reports on the Progress of Chemistry issued by The Chemical Society (London) 1926 and 1927.

Also Hückel (1924) and Noyes (1924).

CHAPTER XXVI

Supplementary Methods

But yet I'll make assurance double-sure.—Macbeth, IV: 1

When the control of any process has been found to be indexed by the activity or concentration of the hydrogen or hydroxyl ions, when the quantitative relations have been established and contributory factors are controllable, there is established a possible means of estimating the activity or concentration of the hydroxyl or hydrogen ions. Many such instances are known. From among them a few may be chosen for their convenience. They are spoken of here as supplementary methods because they are superseded in general practice by indicators, the hydrogen electrode and the quinhydrone electrode. Several have historical value because they were used in establishing the laws of electrolytic dissociation. Others have intrinsic value because they are available either for checking the customary procedures or for determinations in cases where there is reason to doubt the reliability of the usual methods. Those which are kinetic methods will in the end make their distinctive contributions by showing what they can of the correlation of certain kinetic affairs with equilibrium states. Generally they are rather useful to "make assurance double sure."

An instance of the last procedure is the following. Clibbens and Francis (1912) found that the decomposition of nitrosotriacetonamine (see Heintz, 1877) into nitrogen and phorone is a function of the catalytic activity of hydroxyl ions. Francis and Geake (1913) then applied the relation to the determination of hydroxyl ion concentrations, Francis, Geake and Roche (1915) improved the technique, and then McBain and Bolam (1918) used the method to check their electrometric measurements of the hydrolysis of soap solutions.

It is just in such checking that the value of these so called supplementary methods will be appreciated. But, since they will find only occasional use and under circumstances which will require a detailed consideration of their particular applicability, there seems to be no reason to do more than indicate a few of the methods in brief outline.

Among the reactions which have historical interest there are, besides the most frequently studied inversion of cane sugar, the following.

Bredig and Fraenkel (1905) used diazoacetic ester

$$N_2CH \cdot CO_2 \, C_2H_5 + H_2O = N_2 + (OH)CH_2CO_2C_2H_5$$

The nitrogen evolved from time to time was measured and the values used in the equation for a monomolecular reaction. At 25°C., $\dfrac{k}{[H^+]} = 32.5$.

The method was applied with only partial success by Höber (1900) to blood.   Van Dam (1908) used it in the examination of rennet coagulation of milk.

The decomposition of nitrosotriacetonamine is represented in outline by the following equation:

$$CO\diagup\!\!\!\!\diagdown\begin{matrix}CH_2 \cdot C(CH_3)_2\\CH_2 \cdot C(CH_3)_2\end{matrix}\!\!N \cdot NO \rightarrow CO\diagup\!\!\!\!\diagdown\begin{matrix}CH : C(CH_3)_2\\CH : C(CH_3)_2\end{matrix} + N_2 + H_2O$$
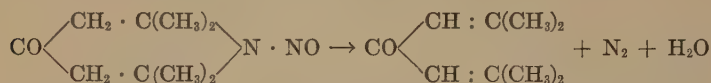
The original quantity of nitrosotriacetonamine is known and the extent of the decomposition at the end of measured intervals of time is measured by the volume of nitrogen evolved.

Francis, Geake and Roche (l.c.) found the relation between the velocity constant and [OH⁻] to be $\dfrac{k}{[OH^-]} = 1.92$ at 30°.   See Colvin (1926).

Brønsted (1926) finds that the rate of addition of water to nitratoaquo-tetramine cobalt ion is very sensitive to the hydrion activity of the solution and suggests the use of the rate in determining hydrion activities.

Numerous other methods are mentioned in the texts of physical chemistry and, now that interest in the theory is reviving, are detailed in current journal articles.

For the most part these supplementary methods are catalytic and involve what are called pseudo-unimolecular reactions.   Consider the reaction

$$A + H^+ \rightarrow H^+ + \text{products}$$
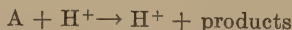
If [H⁺] is maintained constant, as by a buffer solution, the decline of [A] with increase of time may be described by

$$\frac{-d[A]}{dt} = k' [A] [H^+]$$

$$\frac{-d[A]}{[A]} = k' [H^+] dt$$

Treat [H⁺] as constant and integrate between [A]₁ at time t_1 and [A]₂ at time t_2

$$-ln \frac{[A]_1}{[A]_2} = k' [H^+] (t_1 - t_2)$$

If $2.303 \; k' = k$

$$\log \frac{[A]_1}{[A]_2} = k [H^+] (t_2 - t_1) = tk [H^+]$$

Many methods have been used to follow reaction velocities. Among these may be mentioned measurement of the gas evolved, as, for instance, in the decomposition of nitrosotriacetoneamine and the change in optical rotation during the hydrolysis of cane sugar to invert sugar.

Brønsted and King (1925) describe an apparatus suitable for following either the decomposition of nitrosotriacetonamine or any reaction of a similar nature wherein nitrogen is evolved. Their paper should be consulted for a discussion of the manner in which the salt concentration of a buffer solution affects the velocity constant.

The polarimetric method is described as follows by Lamble and Lewis (1915) (see Rice in Taylor's *Treatise*).

Polarimeter tubes 4-dcm. in length were used, surrounded by jackets, through which water at $25° \pm 0.1$ was circulated. 25 cc. of standard hydrochloric acid solution was added to 25 cc. of a 20 per cent solution of sucrose, both solutions being at 25°C., and immediately the mixture was placed in the observation tube; the rotation α_t is noted at convenient time intervals and the final rotation α_∞ is measured after at least 48 hours from the start of the reaction. We can assume that the velocity of the reaction will be proportional to the concentration of the cane sugar and to the concentration of the hydrochloric acid, if the reaction takes place in dilute solution. The velocity equation will be, therefore,

$$[H^+] \; kt \; = \; \log \frac{[A]_1}{[A]_2}$$

where $[H^+]$ is the initial concentration of the hydrochloric acid which remains constant during the experiment, $[A]_1$ is the initial concentration of the cane sugar and $[A]_2$ is its concentration after time t. The ratio is independent of the particular unit of concentration used so that if the rotations are additive we can replace $\frac{[A]_1}{[A]_2}$ by $\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$, where α_0 is the initial rotation and α_∞ is the final rotation. Rosanoff, Clarke and Sibley showed that the specific rotation of the solution is an additive function of its composition and also gave a method for calculating α_0; a slight error in the value of α_0 will be greatly magnified in the value of k calculated for the earlier stages of the reaction, so instead of trying to obtain α_0 by direct observation they extrapolated to $t = 0$ the straight line obtained by plotting values of t against corresponding values of $\log (\alpha_t - \alpha_\infty)$; this gives far more reliable values of $\log (\alpha_0 - \alpha_\infty)$ than can be obtained by direct measurement.

For other methods consult texts of physical chemistry, for example the article by Rice in *A Treatise on Physical Chemistry*, edited by Taylor.

A large proportion of reactions proceeding in homogeneous solutions are catalyzed by hydrion or hydroxyl ions. For this reason emphasis was first placed upon these ions. However, it was soon found that neutral salts when added to solutions of strong acids markedly increase the rates

of such reactions as the inversion of cane sugar. Several theories have been advanced to account for this. Considerable systematic advance has been made by the use of activities in place of concentrations in the equations for reaction kinetics and by the use of the hypothesis that, in the formation of an unstable critical complex between reacting molecules and ions, the charged complex is subject to those interionic forces which markedly affect the activity coefficients. Also catalytic functions are now admitted for ions other than hydrogen and hydroxyl.

In many instances these catalytic methods of determining hydrogen or hydroxyl ion concentrations may be applied with neglect of the salt-effect if only the order of magnitude be desired; but if they are applied for accurate data the current literature should be consulted for important treatments of what is often called the salt effect. See especially Brønsted (1923–1927), Dawson (1926–1927), Scatchard (1926), Kilpatrick (1926), Pedersen (1927) and references to other modern work in Annual Reports on the Progress of Chemistry for 1927, London Chemical Society (1928), pp. 33 and 331.

CONDUCTIVITY

The conductivity of a solution is dependent upon the concentrations of all the ions and upon the mobilities of each. It is therefore obvious that a somewhat detailed knowledge of the constituents of a solution and of the properties of the constituents is necessary before conductivity measurements can reveal any accurate information of the hydrogen or hydroxyl ion concentration. Even when the constituents are known it is a matter of considerable difficulty to resolve the part played by the hydrogen ions if the solution is *complex*. However, the mobilities of the hydrogen and hydroxyl ions are so much greater than those of other ions (see page 279) that methods of approximation may be based thereon. If, for instance, a solution can be neutralized without too great a change in its composition it may happen that with the disappearance of the greater part of the hydrogen ions there will appear a great lowering in conductance. Then, with the appearance of greater hydroxyl ion concentration, the conductance will rise. The minimum or a kink in the curve is a rough indication of neutrality. Thus the conductivity method is sometimes useful in titrations. See Kolthoff for details and references on titration by the conductivity method.

The elementary principles of conductivity measurements will be found in any standard text of physical chemistry but the more refined theoretical and instrumental aspects are only to be found by following the more recent journal literature. See Jones and Josephs (1928).

Of course, the major field of usefulness of the conductivity method has been in the determination of dissociation constants of weak acids.

As mentioned in Chapter XXV, change in the ionic strength of a solution changes the inter-ionic forces which affect the mobilities of ions. Therefore, the original basis for calculating the degree of ionization from the ratio of conductance at one concentration to the conductance at in-

finite dilution must be altered. However, MacInnes (1926) proposes dividing the equivalent conductance of an acid at a given concentration by the equivalent conductance of completely dissociated acid at the same ion concentration. He thereby obtains for acetic acid, for instance, $K_a = 1.743 \times 10^{-5}$ to 1.784×10^{-5}. (A discrepancy of only 0.01 pH unit in the range of concentration 0.07 to 0.002.)

MISCELLANEOUS METHODS

Were it worth while there could be detailed under this heading a wide variety of phenomena which have actually been used to determine approximately the hydrogen ion concentration of a solution. We may instance the precipitation of casein from milk by the acid fermentation of bacteria. This has not been clearly distinguished in all cases from coagulation produced by rennet-like enzymes; but, when it has been, the precipitation or non-precipitation of casein from milk cultures has served a useful purpose in the *rough* classification of different degrees of acid fermentation. In like manner the precipitation of uric acid or of xanthine has been used (Wood, 1903). See also pages 575 and 582.

Many of the physical methods are of considerable interest. For instance the determination of distribution ratios of a given substance between different solvents enters very frequently into the determination of activities and into the determination of hydrion activities. The fact that water completely extracts certain salts from benzene solution has been used as an argument for complete dissociation in the aqueous phase (see for example Hill ('21)). Distribution between liquid and liquid is only a special case of heterogeneous equilibria and if we attempted to discuss even the main principles a chapter of considerable magnitude would soon develop. An exposition of the matter is given in such treatises as that of A. E. Hill in Taylors *Treatise on Physical Chemistry* page 343. Of peculiar interest to biochemistry is the manner in which the distribution of carbon dioxide between the gaseous and the liquid phases enters an equilibrium equation whereby, with the measurement of CO_2 partial pressure and one other quantity such as "total carbonate," the pH value of a bicarbonate solution may be determined. See Chapter XXX under "Blood." Thus the bicarbonate system is made an *indicator* as truly as phenol red is an indicator.

An interesting application of equilibria involving a gas phase is the "electric nose" developed by Hickman and Hyndman (1928). A small amount of ammonium salt is placed in the acid solution which is to be mixed with an alkaline solution. On admixture, ammonia is set free at a partial pressure depending largely upon the pH value of the mixture. This ammonia can be aspirated to a separate aqueous solution the conductivity or reaction of which now becomes a function of the adjustment in the main mixture. A device operating upon the response of this "nose" controls the main mixing.

See also Osterhout (1918) on the use of partial pressures of CO_2 for following respiration.

In the literature are found many and divers interesting, suggestive or obviously cumbersome physical methods. The heat of neutralization of acids and bases and the cessation of heat evolution when, in a titration, neutralization is complete has been put to use by Dutoit and Grobet (1921). Cornec (1913) attempted to estimate the end-point in titrations by changes in refractive indices. His following of the changes in freezing points yielded some interesting curves, for instance that of chromate-bichromate. Windisch and Dietrich (1919–1921) put alteration of surface tensions to use. In this connection we may remark that Harkins and Clark (1925) find that the surface tensions of solutions of sodium nonylate are especially sensitive to changes in pH.

Correlation between changes in optical rotation and pH are discussed briefly in Chapter XXX. In Chapter VII fluorimetry is mentioned.

Taste has its very restricted place.

AN ALTERNATE METHOD OF FORMULATING ACID-BASE EQUILIBRIA

A particular statistical law can have various origins.—GUYE

*"If there's no meaning in it," said the King, "that saves a world
of trouble, you know, as we needn't try to find any."*—LEWIS
CARROLL, in *Alice in Wonderland.*

The usual formulation of acid-base equilibria starts with the consideration of the ionization of the acid or the base. If there is used Brønsted's generalization, namely

$$\text{Acid} \rightleftharpoons \text{Base} + \text{H}^+$$

e.g.
$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$$

or
$$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+,$$

and the equilibrium equation

$$\frac{(\text{Base})\,(\text{H}^+)}{(\text{Acid})} = \text{K}_a,$$

the hydrion appears of importance coördinate with the acid and the base, the acid and the anion or the base and the cation.

Likewise the usual formulation of the equilibrium established at the hydrogen electrode involves the assumption that hydrogen ionizes in the sense of

$$\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\epsilon$$

and that equilibrium between the free hydrions in the electrode and those in the solution is of primary importance. Accordingly the activity of free hydrions appears to be of paramount importance to the operation of a hydrogen electrode, even in alkaline solution. But the activity of hydrions may be as low as 10^{-14}, or less, in alkaline solutions and the concentration of hydrions, calculated in the usual manner,[1] is of that order of magnitude. The opinion has been expressed that the support of stable potentials by hydrions acting at concentrations less than 10^{-10} is not to be expected on grounds of kinetic theory. (See Chapter XVIII.)

Now that N_o, the number of molecules of solute present per liter in a molar solution, is accurately known, it is certain that in a solution having

---

[1] The discussion is not seriously altered by maintaining a meticulous distinction between "activity" and concentration.

a hydrogen ion normality as low as 10^{-13} there are about 10^{10} hydrogen ions per liter. This estimate, when taken in conjunction with the electrical charge associated with each ion, may indicate how it is that a normality of 10^{-13} H^+ may be detected.

But there still remains the fact that this normality is very low in comparison with the other material present even in distilled water. In solutions heavily buffered at pH 13 we find the hydrogen electrode or an acid indicator *rigidly stabilized* in its conduct and it is questioned whether this can be brought about by such extreme relative dilutions of the hydrogen ions alone. Keller (1921) has expressed doubt of another sort. He calls attention to the diminutive size of the hydrogen ion (allowing for hydration) compared with a giant protein molecule, and, picturesquely proportioning the one to the other as a bacterium to a Mont Blanc, he questions the influence upon the protein which is attributed to the hydrogen ion.

All these are "sharp-hooked questions" which, were they "baited with more skill, needs must catch the answer." In many of the answers given there lies an easily detected fallacy. It is that our present convenient modes of formulating relations are regarded as complete pictures of the physical facts and as such are followed to the bitter end with disastrous results. In a previous chapter we have attempted to broaden the outlook just a little, and have suggested that in many cases a more complete formulation of relations would show that as the physical effectiveness of one ion fades out at extreme dilution other components of the solution maintain the continuity. From this point of view even the more extreme "calculation values" retain a definite significance.

We shall show that an extremely low hydrogen ion concentration is significant as an *index* of the state of an equilibrium in which the hydrogen ion itself has little actual physical significance. Its introduction as a component of the equilibrium is a *convenient* and at the same time a stoichiometrically true and mathematically correct mode of expression containing no implications regarding the actual physical effectiveness of a low hydrogen ion concentration as an individual quantity separable from the other components of a solution. At higher concentrations there can be little doubt of the physical effectiveness of the hydrogen ions whatever their size, or energy relative to other bodies. The energy placed on the grid of an electron tube may be small, but the potential of the grid may determine a large flow of energy between filament and plate. The hydrogen ions in a solution may be small in relative size or relative numbers, but they may control the mobilization of a large reserve.

These remarks need not be left in the above form. They may be stated mathematically.

To emphasize one important aspect we shall deal first with acids any one of which is so "weak" that the hydrions which it liberates, when the salt is present in solution, are too few for their concentration to approach the order of magnitude of the concentration of either the acid or of the salt of that acid. Indeed we shall assume that the hydrion con-

centration is so low in comparison with that of any of the chief components of the solution that it may be entirely neglected in approximate equations. We shall then proceed to develop the ordinary equilibrium equations, and shall deal later with the hydrogen electrode,—in each case dispensing with the use of concentrations of free hydrions.

Experiment makes us familiar with the fact that a weak acid may be displaced partially or completely from its salt by certain other weak acids. For instance, consider the reversible reaction between sodium phenolate and acetic acid. Assuming complete dissociation of the salts, we may write the reversible reaction

$$P^- \quad + \quad HAc \quad \rightleftharpoons \quad HP \quad + \quad Ac^-$$

phenolate   acetic acid   phenol   acetate
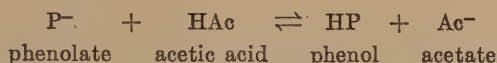
and the equilibrium equation

$$\frac{[P^-] \, [HAc]}{[HP] \, [Ac^-]} = K_{AB} \tag{1}$$

Evaluation of the constant K_{AB} of equation (1) would be of great value in calculating both the direction and the extent of the interaction between the system acetate-acetic acid and the system phenolate-phenol. To make the matter simple assume first that the acetate-acetic acid system is to be used with the initial ratio $\frac{[HAc]}{[Ac^-]}$ at unity and in such relatively large concentrations that the addition of small quantities of phenol or phenolate will not appreciably change the ratio $\frac{[HAc]}{[Ac^-]}$. Were K_{AB} greater than unity, it would signify that the acetate-acetic acid system would convert phenol to phenolate. We know that the conversion is in the opposite direction. K_{AB} is less than unity, indicating the tendency for the conversion of phenolate to phenol. Furthermore, K_{AB} is *much less than unity*, indicating the tendency toward *extensive* conversion. Now consider the converse case in which the phenolate-phenol system is predominant and the ratio $\frac{[P^-]}{[HP]}$ is unity. The fact that K_{AB} is not only less than unity but much less, indicates that the phenolate-phenol system will convert the acetate-acetic acid system extensively in the direction of acetate and not in the direction of acetic acid.

In general the extent of conversion at the attainment of an equilibrium state may be calculated as follows. Introduce the initial values in place of [HAc], [Ac⁻], [HP] and [P⁻]. Use the value[2] $10^{-5.4}$ for K_{AB} and solve the following equation for x, the change between initial and final concentration.

$$\frac{([P^-] - x) \, ([HAc] - x)}{([HP] + x) \, ([Ac^-] + x)} = 10^{-5.4} \tag{2}$$

[2] Approximate value.

In the special case where, initially, $[P^-] = [HAc] = [HP] = [Ac^-]$, equation (2) reduces practically to $x = [P^-] = [HAc]$. Whence the conversion to phenol and acetate is practically complete.

Obviously it would be a great advantage to have a constant comparable with K_{AB} for each system composed of one weak acid and its salt in admixture with another weak acid and its salt. Of course we have data for these; but derived in a way different from that to be discussed. A systematic study of this problem could have been made as follows.

Let us choose as a standard of reference any system of a weak acid and its salt. To be specific let us choose as the standard a solution made with 0.1 mole acetic acid and 0.1 mole sodium acetate per liter of solution.

Add to this standard solution so small a quantity of brom cresol green that it may be assumed not to change appreciably the ratio of acetic acid to acetate. Experiment shows that this indicator is partially transformed by the mixture; while in a solution of sodium acetate it is "blue" and in a solution of acetic acid it is "yellow." Assume that the "yellow" is proportional to the concentration of the acid, HI, and the "blue" is proportional to the concentration of the anion, I^-. Write the equilibrium equation

$$\frac{[HAc]\,[I^-]}{[Ac^-]\,[HI]} = K_{AI} \tag{3}$$

It will be convenient to rewrite (3) in the following logarithmic form:

$$\log \frac{[Ac^-]}{[HAc]} = \log \frac{1}{K_{AI}} + \log \frac{[I^-]}{[HI]} \tag{4}$$

When we have the selected standard condition, namely $\dfrac{[Ac^-]}{[HAc]} = 1$,

$$\log K_{AI} = \log \frac{[I^-]}{[HI]} \tag{5}$$

Now the ratio $\dfrac{[I^-]}{[HI]}$ can be determined colorimetrically by the Gillespie method (See Chapter VI). This experimental datum being determined, K_{AI} is made known.

Next proceed to vary the ratio $\dfrac{[Ac^-]}{[HAc]}$ and in each instance to determine colorimetrically the ratio $\dfrac{[I^-]}{[HI]}$. With the aid of (4) chart the results as shown in figure 91. There the ordinates are $\log \dfrac{[Ac^-]}{[HAc]}$ and the abscissas are percentage salt formation—in this first instance that of brom cresol green.

Next proceed with brom cresol purple in the acetic acid-acetate mixtures. In this instance we encounter some experimental difficulty because it is impossible to produce a high percentage of salt formation with

brom cresol purple without using such high values of the ratio $\frac{[Ac^-]}{[HAc]}$ that exact knowledge of the values of this ratio are subject to considerable uncertainty because of experimental errors. Nevertheless a considerable portion of the complete data may be obtained experimentally and written into the equation

$$\log \frac{[Ac^-]}{[HAc]} = \log \frac{1}{K_{AI'}} + \log \frac{[I'^-]}{[HI']} \tag{6}$$
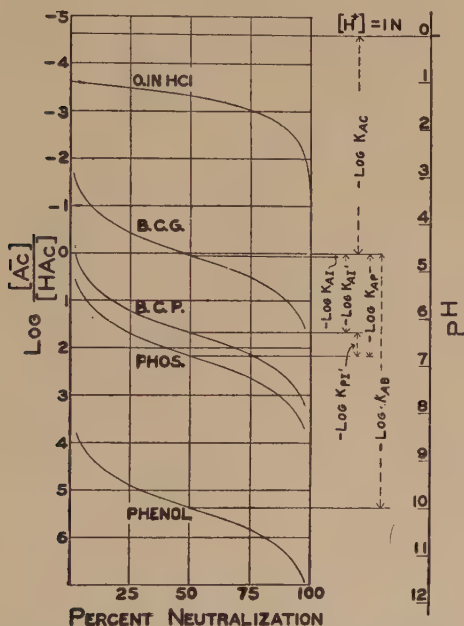
FIG. 91. APPROXIMATE DESCRIPTION OF ACID-BASE EQUILIBRIA BY REFERENCE TO 0.1 M ACETIC ACID + 0.1 M SODIUM ACETATE AS STANDARD OF REFERENCE

Subsequent alignment with usual pH scale

Here HI' and I$^{-\prime}$ refer to brom cresol purple and its anion respectively, and $K_{AI'}$ is the equilibrium constant for the reaction

$$HAc + I'^- \rightleftharpoons HI' + Ac^-$$

The results are charted in figure 91.

Although there was difficulty in using the acetic acid-acetate mixtures to produce a wide range of transformation in brom cresol purple, it is found

experimentally that no such difficulty arises when mixtures of KH_2PO_4 and Na_2HPO_4 are used. We shall then have the equilibrium equation

$$\log \frac{[HPO_4^{--}]}{[H_2PO_4^{-}]} = \log K_{PI'} + \log \frac{[I'^{-}]}{[HI']} \tag{7}$$

Combine equations (6) and (7)

$$\log \frac{[Ac^{-}]}{[HAc]} = \log \frac{1}{K_{AI'}} + \log \frac{1}{K_{PI'}} + \log \frac{[HPO_4^{--}]}{[H_2PO_4^{-}]} \tag{8}$$

When $\dfrac{[HPO_4^{--}]}{[H_2PO_4^{-}]} = 1$, we have:

$$\log \frac{[Ac^{-}]}{[HAc]} = \log \frac{1}{K_{AI'}} + \log \frac{1}{K_{PI'}} = \log \frac{1}{K_{AP}} \tag{9}$$

In (9) the constant K_{AP} has been substituted for the product $K_{AI'} K_{PI'}$. The significance is made clear in figure 91.

It is unnecessary to proceed further with the detail of such a development. What has been given briefly is sufficient. By selecting some solution of a weak acid and its salt as a standard of reference, and by comparing other systems of weak acids and their salts with this standard (either directly or indirectly) it is possible to systematize equilibria in terms of the standard of reference.

We find in figure 91 that the system phenol-phenolate is charted with ordinate $\log \dfrac{[Ac^{-}]}{[HAc]}$. There should be no difficulty in appreciating how, by the use of intermediate systems, the placement of this system could be found and there should be no doubt of the real value of such data. Yet someone might note the very large value of $\log \dfrac{[Ac^{-}]}{[HAc]}$ when phenol is 90 per cent neutralized and might object that such a value can have no physical significance. Such an objection would be quite comparable with *one* objection to the use of large values of pH. But, should the occasion arise, the objector would not hesitate to use the equilibrium constants indicated in figure 91 to calculate the extent of a change in a given phenol-phenolate system produced by the addition of a given mixture of primary and secondary phosphates.

However, the objection to employing these "calculation values," expressed in terms of a *particular* system, can be removed. Our present interest is only in the *relation* of one system of a weak acid and its salt to another system of a weak acid and its salt. The *relative* position of each of the systems shown in the figure (or of any other system we may wish to include) is our only concern. This *relative* position will not be changed if we preserve the same numerical scale for the ordinate but change the

origin.   One might add the constant 777 and call the ordinate the axis of pQ. A *distance* between the centre points of any two curves would remain the same and would be the negative logarithm of the equilibrium constant for the reaction *between the two systems described by those curves.*

By considering the brom cresol green system to be the temporary working standard we would be able to work out the curve for the acetic acid-acetate system.   To avoid confusion this has not been included in the figure, the ordinate of which is $\log \frac{[Ac^-]}{[HAc]}$.

If, for purposes of illustration, we continue to use approximate equations, we can easily introduce into this scheme of presentation the case of any acid which directly furnishes appreciable concentrations of hydrogen ions.

Consider the equilibrium between hydrochloric acid and the acetate-acetic acid system.

The equilibrium for the reaction

$$Na^+ + Ac^- + H^+ + Cl^- \rightleftharpoons Na^+ + Cl^- + HAc$$
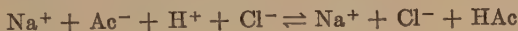
is expressed by

$$\frac{[Ac^-]\,[H^+]}{[HAc]} = K_{Ac}$$

or

$$\log \frac{[Ac^-]}{[HAc]} = \log \frac{1}{[H^+]} - \log \frac{1}{K_{Ac}} \qquad (10)$$

When we choose the standard state, namely $\frac{[Ac^-]}{[HAc]} = 1$, we find

$$\log \frac{1}{[H^+]} = \log \frac{1}{K_{Ac}} \qquad (11)$$

We need not pause to outline direct, or intermediate, means whereby equation (10) can be experimentally studied, or how the value 4.63 for $-\log K_{Ac}$ is reached.   Assuming that this relation is determined, apply (10) to the case of 0.1 N hydrochloric acid during titration with sodium hydroxide.   Assume that at each stage of this titration the concentration of residual hydrochloric acid equals $[H^+]$.   The "titration curve" is plotted in figure 91 with the aid of (10).   For example, at half-neutralization $[H^+] = 0.05$ or

$$\log \frac{[Ac^-]}{[HAc]} = \log \frac{1}{0.05} - 4.63 = -3.33$$

With any given value of $[H^+]$ established, it is now possible to reconstruct the scale of the ordinate in terms of pH.   See this scale at the right of figure 91.

The development given above is so obvious in its outline that perhaps some of the detail was unnecessary. From the main theme we may draw these conclusions. No physical effectiveness of extremely small hydrion concentrations need be sought and no particular virtue need be attached to a standard of reference so long as we are concerned only with the approximate equations expressing equilibria in mixtures of weak acids and their salts.

When exact formulation is undertaken there apply to the equations given above the same *type* of correction for departure from the laws of the ideal gas that have been discussed in previous chapters; but in some instances different standards of reference would be used.

There remains a matter of some physical significance. The scheme outlined in this chapter implies that ionization of a weak acid is not a necessary preliminary to reaction but that a reaction can proceed in the sense:—

$$HA + R^- \rightleftharpoons HR + A^-$$

i.e., by direct transfer of a hydrion from the molecule of one species to the anion of another species. There is no reason to suppose that this is the exclusive process any more than there is reason to believe that preliminary ionization is necessary. There is reason to believe free hydrions to be present in solutions of acids as "weak" as acetic. Historically such cases became prototypes the conduct of which has been extrapolated to cases in which there is no direct evidence of free hydrions. So far as the author knows there is no way to call forth the characteristic "acid" properties of extremely weak acids except to attack them with bases. Then the formulation can legitimately follow that outlined, not necessarily in experimental procedure, but rather in the interpretation which does away with the necessity of thinking in terms of hydrion concentrations.

However the customary formulation with the use of pH values is by far the *more convenient*.

Now consider the hydrogen electrode, which is usually regarded as a means of measuring the activities of free hydrions.

As usual, assume that at the electrode hydrogen ionizes to protons and electrons. In a solution of a strong acid containing only the ions of the acid and no undissociated acid molecules, we very naturally assume that the equilibrium potential is determined by the distribution of hydrions between solution and electrode. The assumed scheme is successfully extrapolated to apply to the conduct of an electrode in a solution containing a weak acid and its salt, the calculated hydrion activity being in some cases as low as 10^{-11}, or less.

We may equally well assume that the electrons arising from the ionization of the hydrogen attack the peripheral protons of the weak acid *directly*. Idealizing the reaction as

$$2HA + 2\epsilon \rightleftharpoons H_2 + 2\,A^-,$$
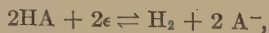
and proceeding to the formulation of the potential at a single electrode by the method of Chapter XVIII we have equation (12)

$$E = E_o - \frac{RT}{F} \, ln \, \frac{(A^-) \, \sqrt{P}}{(HA)} \tag{12}$$

In (12) P is the pressure of hydrogen in atmospheres. Hereafter we shall maintain this pressure at one atmosphere and so eliminate P from the equations.

If one hydrogen electrode is immersed in a solution of acetic acid and sodium acetate and another hydrogen electrode is immersed in a solution of primary and secondary alkali phosphates, if the solutions are joined and liquid junction potential is supposed to be eliminated, we have:

$$E.M.F. = E_A - E_P + \frac{RT}{F} \, ln \, \frac{(HAc) \, (HPO_4^{--})}{(Ac^-) \, (H_2PO_4^-)} \tag{13}$$

Now choose the solution which is 0.1 M with respect to acetic acid and 0.1 M with respect to sodium acetate as a standard of reference. Also assign to E_A (which is the single potential for the equimolecular mixture) the arbitrary value 0. Also when the potential of the cell under consideration, or any other cell, is referred to this standard let the reference be shown by the subscript "a" in E_a, the electromotive force of the cell.

Then equation (13) becomes:

$$E_a = E_P - \frac{RT}{F} \, ln \, \frac{(HPO_4^{--})}{(H_2PO_4^-)} \tag{14}$$

When $\dfrac{(HPO_4^{--})}{(H_2PO_4^-)} = 1$, we have

$$E_a = E_P$$

Without being shown the detail, the reader will at once perceive that by constructing cells one half of which contains the standard acetate solution and the other half of which contains in succession mixtures of weak acids and their respective salts we can construct a systematic chart of equilibrium relations comparable with figure 91.

It is also evident that any standard of reference can be chosen, for instance the calomel half-cell. Such changes of reference are similar to the addition of a constant quantity to each value on the ordinate of figure 91 discussed previously.

But of more importance is it to note that we need not specify the electrode process. We may simply specify that we are dealing with some process by which the weak acid is converted to its anion. Consider any half-cell as the standard of potential reference. The process at this half-

cell need not be known. Use the subscript "s" to show reference to this standard. It was suggested above that the reference can have any value. We shall then still have the relation

$$E_s F = E F - RT \, ln \, \frac{(A^-)}{(HA)} \tag{15}$$

This formulates the free energy change in the transformation of a mole of an acid to a mole of the corresponding anion by some process, *standard*, but *of unknown nature*. Evaluations have a most obvious use for they enable one to calculate the direction and extent of the conversion of one acid into its salt by another system of an acid and its salt.

We have already stated that a hydrogen electrode in a solution of hydrochloric acid can be considered most reasonably as functioning in response to free hydrions. If such a solution of hydrion activity of unity is made the standard of reference and if the process at the other electrode is considered to be

$$2HA + 2\epsilon \rightleftharpoons H_2 + 2A^-$$

we can formulate the potential of the cell, as mentioned previously, by the method of Chapter XVIII and so obtain (when the hydrogen pressure on both sides is unity):

$$E_h = E_o - \frac{RT}{F} \, ln \, \frac{(A^-)}{(HA)} \tag{16}$$

or in numerical form for 25°C.

$$\frac{E_h}{0.059} = \frac{E_o}{0.059} - \log \frac{(A^-)}{(HA)} \tag{17}$$

It will now be remembered that a value of pH as actually determined is none other than $-\dfrac{E_h}{0.059}$. The constant $-\dfrac{E_o}{0.059}$ would, by any other name be a constant still. Call it pK. Then equation (17) may be written as (18)

$$pH = pK + \log \frac{(A^-)}{(HA)} \tag{18}$$

This is, of course, the familiar Henderson-Hasselbalch equation in terms of activity. It was derived by using the customary standard of reference which implies the participation of free hydrions in that half of the cell which is the standard half-cell; but it is now implied that in that half-cell which is of particular interest no appreciable quantities of free hydrions need be present.

The above outline should not be interpreted as meaning that no hydrions are present in solutions buffered by very weak acids and their salts. In-

deed the complete equations would take into consideration both hydrions and hydroxyl ions. These components would then be of *particular* importance in very acid or very alkaline solutions, of *relatively negligible* importance in "neutral" solutions and in the intermediate zones they would rise or fall in their importance according to the concentrations and states of equilibria of the components of a solution. Here we are probably dealing with a class of cases in which the physical effectiveness of one or another species dwindles gradually as conditions change and while the dwindling occurs other species take up and maintain the continuity of effects.

The above outline has no advantage over the usual presentation. Indeed it is clumsy because no advantage has been taken of the common component of acid-base equilibria, namely the hydrion. Use of the hydrion concentration or activity makes the ordinary presentation direct and elegant. The purpose of the alternate presentation is to convince the elementary student that the extremely small "calculation" values he is asked to use are truly indices of positions of equilibria among relatively large quantities of material. It then appears that he is dealing with a problem in the *organization* of his experimental facts. Furthermore the alternate method, in spite of its formality, may help to dispel illusions which some writers have introduced into a comparatively simple set of formulations. For instance Dixon (1927) uses, as the keynote of an argument on mechanism, the assumption that the hydrogen electrode actually functions in the way ordinarily described. He does not tell his reader that the ordinary description, although an invaluable convenience, is not necessary even to the formulation of acid-base equilibria.

One suggestion of possible value comes from the use of the alternate formulation. Suppose an event involving *kinetics* is *apparently* under the control of the hydrion concentration as ordinarily described. If the apparent critical range is say 5–6 on the pH scale, may it not obscure insight to say that the event "is *controlled* by the hydrogen ion concentration?"

CHAPTER XXVIII

Elementary Theory of Titration

In figure 92 are shown titration curves of hydrochloric acid at two concentrations and titration curves of acetic and boric acids. In each case the curve has been extended to reveal its course when excess alkali is added. The abscissa of the figure is made percentage neutralization for a purpose which will appear presently. In the construction of the curves volume changes are neglected for purposes of simplicity.

Neglect for the moment the curve for the more dilute solution of hydrochloric acid. Consider the nature of the end-points in the other three cases.

When all but a very small part of the hydrochloric acid has been neutralized there comes an approach to what appears, in practicable operations, to be a sharp "break" in the titration curve. On the addition of the last trace of base required for complete neutralization the pH value of the solution plunges to the alkaline region. Much the same sort of phenomenon occurs in the titration of acetic acid; but it is important to note that the range of pH values, compatible with a negligible error in the estimation of the true end-point, is now much narrower. As shown by the figure no significant error would be made were the hydrochloric acid solution which is under consideration to be titrated to pH = 6.0; while a very considerable error would be made were the acetic acid solution to be titrated to this value. In the case of boric acid there is no precipitous change of pH at the end-point. Consequently a high, and almost impracticable, accuracy would be required in titrating to an exactly determined pH value.

In the titration of the more dilute solution of hydrochloric acid the latitude allowable has constricted and again a very high accuracy in the attainment of an end-point pH-value is required.

Theoretically any method which reveals the pH value of the correct end-point and which does not seriously interfere with the equilibria involved can be adapted to the purposes of titration.

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However the hydrogen electrode and indicator methods are most widely used. Of these the indicator method is best adapted to the ordinary work of the analytical laboratory.

It is obvious that, having selected the stoichiometric *percentage neutralization* as the abscissa of figure 92, we may place in this figure the independent titration curve for a very dilute solution of an indicator just as we placed in the same figure the
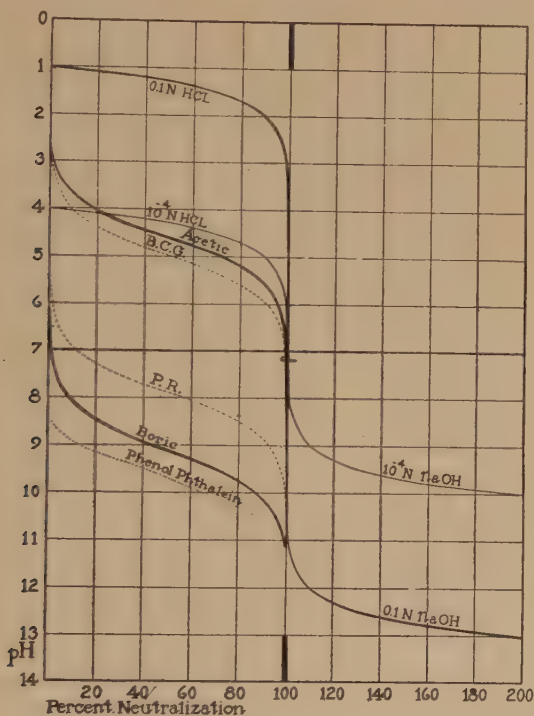
Fig. 92. Titration Curves

titration curve for a very dilute solution of hydrochloric acid. Moreover such a curve for the high dilutions usually employed is practically the same as the curve relating the percentage apparent dissociation (and consequently percentage color transformation) to pH. Furthermore no large error is made if it be assumed that the indicator when present in a solution of the acid being titrated does not displace the titration curve of that acid. Then the

buffer system (titrated acid + salt of the acid), by determining the value of pH, determines the degree of color developed in the indicator. (See Chapters I and V).

As shown by figure 92, either brom cresol green or phenolphthalein could be used as end-point indicator in the titration of tenth normal hydrochloric acid, because at, or extremely close to, the completion of neutralization the value of pH sweeps through the whole range of brom cresol green and well into the range of phenolphthalein. On the other hand the dissociation constant of acetic acid is so low that the flat portion of the curve for acetic acid lies in the region of partial color-transformation of brom cresol green and only gradual color transformation is observed with no satisfactory large change at the end-point. The use of phenolphthalein is indicated in this case.

As already noted the requirement in the case of boric acid is so strict that boric acid is considered to be an untitratable acid until by a curious combination with glycerine it is made a stronger acid. It is not so generally realized that at high dilutions a similar restriction is placed on the titration of an acid even so strong as hydrochloric.

The principles thus briefly outlined apply to the titration of bases with strong acids, but, of course, with the direction of pH change reversed and with the end-points tending to lie on the acid side of pH 7.0. A hydrogen ion concentration of 10^{-7} N or pH 7.0 is called the neutral point because it is the concentration of both the hydrogen and the hydroxyl ions in pure water; but evidently it is seldom the practical or the theoretical point of neutrality for titrations.

The problem of titration with weak acids or bases as reagents is complicated and by reason of the ever shifting end-points required in passing from case to case and the very narrow limits, the practice is to be avoided.

With this brief outline in mind the reader will do well to study the classic paper of A. A. Noyes, *Quantitative Application of the Theory of Indicators to Volumetric Analysis* (*J. Am. Chem. Soc.* *32*, p. 815, 1910) · and the monograph by Niels Bjerrum, *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen* (*Sammlung chem. chem.-tech. Vorträge*, *31*, p. 1, 1914). Much less elegant than the treatments there found, but more condensed, is the following.

In Chapter I there was developed an equation relating all the components of a solution containing a univalent acid and a univalent strong base. That equation is

$$\frac{[H^+]\left([B^+] + [H^+] - \dfrac{K_w}{[H^+]}\right)}{[Sa] - [B^+] - [H^+] + \dfrac{K_w}{[H^+]} - [s]} = K_a$$

This was derived by means of the classic equations which do not hold accurately. Tentatively we shall neglect this aspect and shall return to it later.

It will be in accord with modern tendencies to consider $[s]$, the concentration of undissociated salt, negligible under most but not all circumstances.

Consider first the situation obtaining under ideal conditions when at the true end-point of a titration exactly equivalent amounts of acid $[Sa]$ and total base (equal to $[B^+]$) are present. Then the equation reduces to

$$\frac{[H^+]^3 + [Sa][H^+]^2 - K_w[H^+]}{K_w - [H^+]^2} = K_a$$

Although it is impracticable to solve this equation for $[H^+]$, it is practicable to proceed by either of two methods. In the first, there are introduced assumed values of $[Sa]$ and $[H^+]$ and the equation is solved for K_a. With a sufficient number of such numerical solutions of the equation there can be drawn up a table (or chart) showing the ideal values of $[H^+]$ (or pH) for various values of $[Sa]$ and K_a. By the second procedure use is made of the fact that in numerical solutions of the equation with values ordinarily encountered the terms $[H^+]^3$ and $K_w[H^+]$ usually can be neglected without serious error. As a consequence there may be used within proper limitations the expression;

pH (of ideal end-point) $= \frac{1}{2}[\log([S_a] + K_a) - \log K_a K_w]$

Either procedure leads to data for figure 93.

Figure 93 may be used in the following manner. Given the value of K_a of the acid to be titrated, note the corresponding diagonal in the figure and follow it to its intersection with the

line indicating the concentration of the salt at the final volume. Then read upon the abscissa the ideal value of pH for the end-point.

In the figure the diagonals have been continued only to the heavy, interrupted line signifying the limit for 0.1 per cent error of excess base. The position of this line is *roughly* determined as follows.

Suppose a solution normal with respect to the final concentration of the salt formed is over-titrated so that there is present 0.1 per cent excess base. Assume that this excess base produces a solution of the same pH value as that of a pure water solution containing this same amount of completely dissociated base alone. Obviously the solution then will be 1×10^{-3} normal with respect to hydroxyl ions or, if $pK_w = 14$, the pH value will be 11.0. Repeat this calculation with other cases. There is thus determined the position of the line in question.

For instance, assume that there is to be titrated a solution of an acid with K_a value 1×10^{-4} and that the concentration of the salt at the end-volume is to be 0.1 normal. The ideal value of pH at the end-point is shown by the chart to be 8.5 but if an error of 0.1 per cent excess base is to be allowed the pH value can be 10. Likewise for a final solution of 0.01 normal salt an acid of $K_a = 1 \times 10^{-5}$ should be titrated ideally to pH = 8.5 with a limit at pH = 9.0.

The figure does not show directly the limiting values of pH for errors due to insufficient base. However, as suggested by figure 92 the full curve is so nearly symmetrical with respect to the end-point that the "acid limit" is about as far displaced in one direction from the true end-point as the excess base limit is displaced in the other direction.

For example if $K_a = 10^{-4}$ and $[S] = 0.01$ N the ideal end-point is pH = 8.0 and the limits for 0.1 per cent error excess base or insufficient base are respectively pH = 9.0 and pH = 7.0.

The error of the approximate treatment increases with the dilution of the solution and the pK_a value of the acid being titrated. It becomes obvious in the extreme cases where the optimal end-point is shown as identical with the limit for 0.1 per cent error. However, the chart can still be interpreted to mean that in these extreme cases an impracticable accuracy would be required, for instance with 0.01 N and $K_a = 10^{-6}$ or with 0.1 N and $K_a = 10^{-7}$.
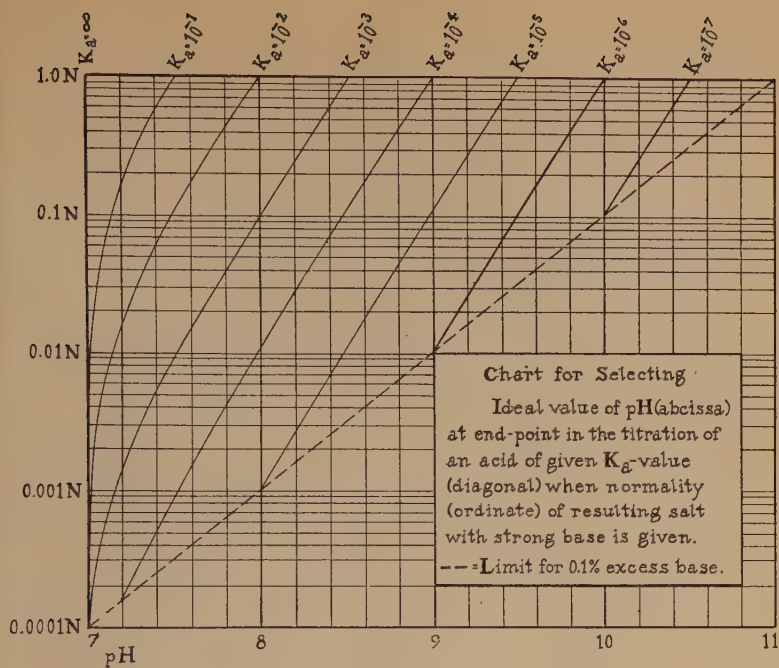
FIG. 93
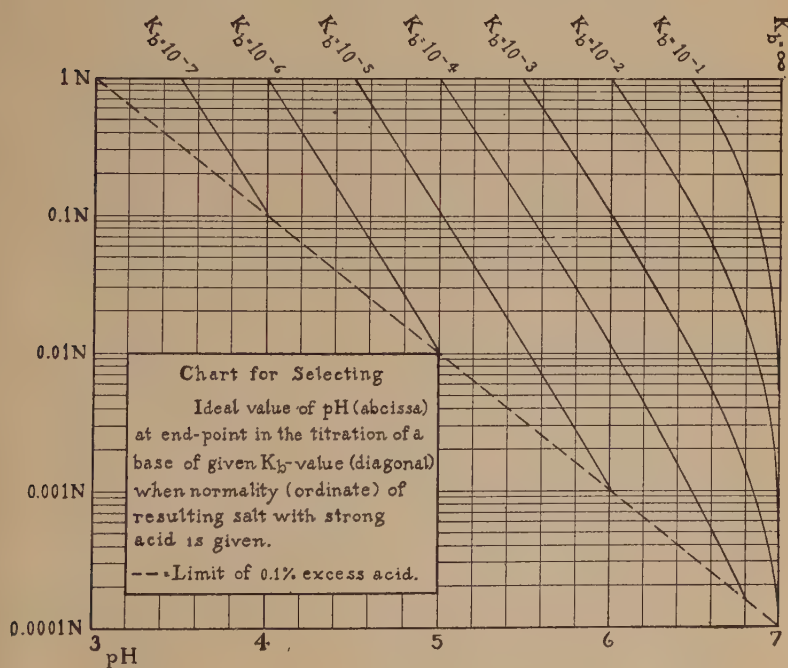
FIG. 94

In an analogous manner there can be developed the chart show-ing the ideal end-points for the titration of bases of various values of K_b, and showing the limits for 0.1 per cent excess acid.   This chart is shown in figure 94.

In the titration of multi-acidic acids it usually occurs that the first and second dissociation constants are sufficiently different in magnitude to make the end-point at the completion of the last stage of the titration that which it would be were there being titrated a univalent acid having the dissociation constant of the last step in the titration of the multivalent acid.   Consequently the principles already developed can be extended and extended not only to the complete titration of multivalent acids but also to the titration of multivalent bases.   However, it is well to bear in mind an item often overlooked.   In searching tables of disso-ciation constants one will frequently find that the constants for the distinctively strong groups of a given acid or base are the only constants given.   It may be that nothing is said about the weaker groups; yet it may well be that one or another of these weak groups begin to function at the higher alkalinities to which it is often necessary to titrate the stronger groups.

Since the error in the titration of small amounts of acid or base becomes larger the higher the dilution, Rehberg (1925) advises the use of low dilutions.   The resulting small volume will then throw the error upon the volumetric apparatus and to meet this Rehberg advocates micro volumetric methods.   This is a deduction from the theory which is of great practical importance.

Modification of the theory must be introduced if account is to be taken of the effects of neutral salts.   In the first place the presence of neutral salts will shift the equilibria in such a way that the stoichiometric end-point is at a value of $[H^+]$ or at a value of the hydrion activity somewhat different than that calcu-lated by means of the classic equations.   In the second place the color of an indicator used to detect a given end-point will be somewhat different than that calculated by means of the classic equations with the aid of constants determined for one environ-ment (e.g., standard buffer solutions).   However, we have al-ready noted the considerable latitude usually allowed and we have seen that this latitude becomes narrow only for extremely weak acids and bases or for very dilute solutions.   Therefore, if

the tendency of the operator is to keep his end-points near the ideal values he need worry little about the effects of neutral salts except in the extreme cases or for the very highest precision. When he does meet the cases requiring exceptional care he is presented with a situation which may be one of such a variable class that a general formulation is hardly practicable. Indeed it would not be permissible to use dissociation constants determined for only one set of conditions.

There is one set of cases where the matter becomes of some importance to common practice. Frequently the occasion arises in which it is desired to titrate a multivalent acid to some intermediate salt, for instance phosphoric acid to NaH_2PO_4. It could be assumed with very good approximation that the classical equations apply. Then there is easily calculated the desired pH value when pK_1 and pK_2 are known. But for high accuracy the complete equations are necessary.

With this very brief outline of the main features we may turn again to the selection of indicators. In a more elegant presentation of the theory of titration, consideration should be given to such matters as the more favorable degree of transformation of an indicator which is to be used as end-point indicator. However, it seems to me to be adequate for most purposes to let the ideal and limiting end-points graphically exhibited in figures 93 and 94 be the guides and in specific applications to select the proper indicator either by the aid of the color chart (page 65), or, under more exacting conditions, to set up a standard color to which to titrate by means of the selected indicator and standard buffer solutions.

From the general form of a titration curve it is evident that the difference of potential between similar electrodes in solutions which differ always by a fixed amount in the degree of neutralization varies with the degree of neutralization and attains a maximum at the end-point. Cox (1925) put this principle to instrumental use in the following way. He divided the solution to be titrated, placed one aliquot in one beaker and another in a second beaker, connected the two solutions with a wet filter paper and proceeded to titrate with two burettes keeping the interval of the amounts added from each burette 0.2 cc. At the end-point the difference of potential between the two electrodes reaches a

maximum. MacInnes and Jones (1926, 1927) simplified the procedure by an ingenious device so that only one burette is necessary. They *shelter* one electrode of figure 95. It will not immediately attain the potential of the other as reagent is added. At the end-point the difference of potential between the two will rise
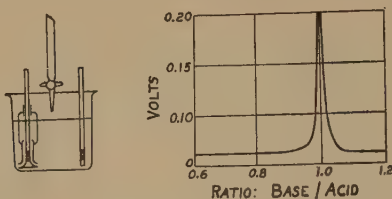
Fig. 95. MacInnes and Jones' Sheltered Electrode for Titration and Typical Course of the Change of Potential between the Sheltered and Unsheltered Electrodes during a Titration

to a sharp maximum. MacInnes analyzes the theoretical error due to this arrangement and concludes that, with the dimensions of the shelter he employs, "the method is capable of high accuracy and is applicable in every case in which a potentiometer technique is possible."

For discussion of potentiometric methods applied to titration in general see: Müller (1926), Kolthoff and Furman (1926), Popoff (1927).

CHAPTER XXIX

Non-Aqueous Solutions

Indeed water is not our sole reliance; hundreds of solvents stand us in good stead to effect electrolysis, and among these are solvents which bring about the ionization of salts as extensively as water—or even more extensively.—Free Translation of P. Walden.

The main principles discussed in the preceding chapters should apply to non-aqueous solutions, except in so far as quantities peculiar to water, for example, K_w, and numerical values applicable to water solutions are concerned. On the other hand we do not have the extensive data which permit so comprehensive a treatment as that accorded aqueous solutions.

From one point of view each solvent is worthy of a separate treatment comparable with that accorded water solutions. If so, individual standardization of activities might be undertaken without reference to intercomparisons. As one of several examples of such independent studies there may be cited Danner's (1922) investigation of the cell:

$$Pt, H_2 \mid HCl, HgCl \mid Hg$$

with ethanol as solvent, and Scatchard's (1925) treatment of this and other studies.

However, when we pass from consideration of the solvent, water, which has attracted most attention, to a consideration of "miscellaneous" solvents, intercomparison becomes the more interesting. If the point of view of intercomparison is taken, a most important caution needs statement at the very beginning. Let us put it in the following manner.

We have seen that the greater part of our data for aqueous systems rests upon use of "concentration cells" which, granting certain assumptions in regard to liquid junctions, determines the free energy of transport of hydrions between two solutions. As a reference there is used a theoretical standard of activity or, practically, a solution of hydrochloric acid which for simplicity we shall now say has a hydrion activity of unity. But it was more

or less immaterial to the purposes of the preceding chapters to specify the state of the hydrion. It was even said that we would agree to ignore the hydration. It is highly probably that in aqueous solutions there are few anhydrous hydrions, H^+, and that the hydrions are largely hydrated,[1] e.g., H_3^+O (see Brønsted, 1927 and Schreiner, 1922–1924). If then we have a cell of the following type

Pt, H_2 | Aqueous solution   ‖ Non-aqueous solution | Pt, H_2
       | hydrion activity = 1 ‖   of an acid
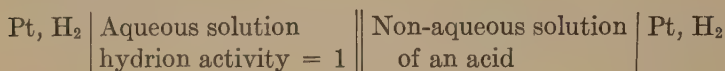
the transport of "hydrions" might well involve a large quantity of free energy in the exchange of the solvents of solvation.

We can avoid this mechanistic conception and can still choose the aqueous system as a standard and say that the activity of the hydrion is unity in the non-aqueous solution when the potential of the above cell is zero.

Nevertheless, in practice, we still have the liquid junction potential which was eliminated from consideration in the above discussion. Suppose two solvents are in junction. Suppose these solvents are miscible to only a slight extent so that two contiguous phases may be established in equilibrium. It is convenient to regard the ions in solution to have individual distribution coefficients and in general to be distributed between the two solvents in such proportions that there will be a potential difference at the interface. This potential difference is now a constraint which has its part in determining the escaping tendencies of the ions. When the potential of the above cell (*with* actual liquid junction) is zero, it does not mean that the two electrode potentials are the same. Hence the application of the above definition of unit activity for the non-aqueous phase would imply some means of eliminating the phase boundary potential.

The so-called phase boundary potential at equilibrium is not to be confused with the potential arising from unequal rates of migration of ions between contiguous but miscible solvents as discussed in Chapter XIII. Phase boundary potentials may be very large.[2]

As set forth in Chapter XXVII, the *approximate* equations of

[1] An extensive review of the literature on ion hydration up to 1922 is given by Fricke (1922).

[2] For discussion see Michaelis and Perlzweig (1926).

acid-base equilibria are valid when there is chosen any arbitrary reference and for many purposes the study of non-aqueous solutions by the potentiometric method may well proceed with the use of any standard of potential. One further caution is then necessary. As D, the dielectric constant of the solution, decreases, the correction term or, $-\log \gamma_i$, increases as shown by inspection of equation 25, Chapter XXV.* Consequently the apparent dissociation constants of acids in non-aqueous solution should change more rapidly than in aqueous solutions with change in the ionic strength of the solution. With few exceptions the dielectric constants of non-aqueous solvents are much smaller than that of water. The following values are approximate.

SOLVENT (LIQUIDS)	DIELECTRIC CONSTANT
HCN	95
Water	81
Glycerol	56
Ethanol	21
Acetone	21
Ammonia	21 $(-34°)$
Glacial acetic acid	10
Benzene	2
Hexane	1.9
(Air)	1.0006
(Vacuum)	1.0

Before proceeding it will be well to mention the advantage, in this field, of a formulation of acid-base equilibria developed by Adams (1916), Michaelis (1914), Bjerrum and particularly Brønsted (1923).

Let there be a substance S which can liberate a hydrion

$$S \rightleftharpoons B + H^+ \qquad (A)$$

Examples are

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
acetic acid   acetate

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$
ammonium   ammonia

$$COOHCOO^- \rightleftharpoons COO^=COO^- + H^+$$
1st oxalate anion   2nd oxalate anion

$$NH_2C_6H_4C_6H_4NH_3^+ \rightleftharpoons NH_2C_6H_4 \cdot C_6H_4NH_2 + H^+$$
1st benzidine cation   benzidine
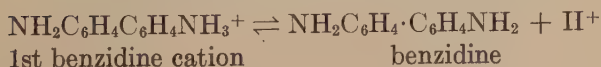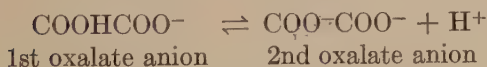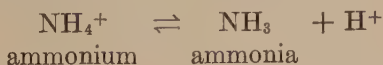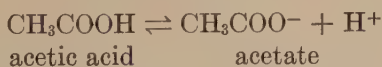
* For an extreme see Schreiner and Frivold (1926).

By this scheme one avoids the *formal* inclusion of the solvent as, for instance, in the formulation of ammonium: ammonia equilibria. See page 48. One may then write in general for a reaction of type A, above:

$$\frac{(B)\,(H^+)}{(S)} = K_a$$

or

$$\frac{(S)}{(B)\,(H^+)} = K_b$$

where K_a is called the dissociation constant of an acid and K_b the association constant of a base.

It is confusing to name cations, anions and undissociated molecules in the way Brønsted does below.

$$NH^+ \rightleftharpoons NH_3 + H^+$$
$$\text{acid} \qquad \text{base}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$\text{acid} \qquad\qquad \text{base}$$
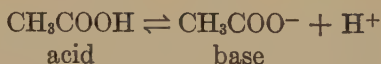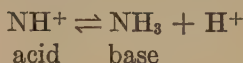
The formal scheme he proposes is convenient and illuminating and can be used without the new names.

While thermodynamic methods are not concerned with mechanism, it is profitable to reconsider the formulation of acid-base equilibria with regard to the solvent concerned.

In formulating the equilibrium state for the ionization of an acid

$$HA \rightleftharpoons H^+ + A^-$$

we wrote

$$\frac{(H^+)\,(A^-)}{(HA)} = K_a$$

We could have assumed interaction with water

$$HA + H_2O \rightleftharpoons H_3^+O + A^-$$
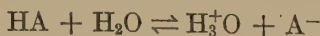
and could have written

$$\frac{(H_3^+O)\,(A^-)}{(HA)\,(H_2O)} = K$$

or if (H_2O) is considered constant

$$\frac{(H_3^+O)\,(A^-)}{(HA)} = K_{aw}$$

H_3^+O is called the "oxonium" ion when there is occasion to distinguish this hydrion from H^+, the proton. Likewise for an acid in any solvent, the activity of which is considered constant, we may write:

$$\frac{(H\overset{+}{s}ol)\,(A^-)}{(HA)} = K_{as} \tag{1}$$

Here $H\overset{+}{s}ol$ represents the solvated proton.

Now suppose a base B to be added to the acid solution and to react according to
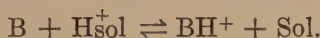
$$B + H\overset{+}{s}ol \rightleftharpoons BH^+ + Sol.$$

Considering (Sol) a constant we have

$$\frac{(B)\,(H\overset{+}{s}ol)}{(BH^+)} = K_{bs} \tag{2}$$

Combination of (1) and (2) gives

$$\frac{(BH^+)\,(A^-)}{(B)\,(HA)} = \frac{K_{as}}{K_{bs}} \tag{3}$$

which is the equilibrium equation for

$$B + H\,A \rightleftharpoons BH^+ + A^-$$

At equilibrium the extent to which this reaction will have proceeded from left to right, as written, may now be described by the ratio $\dfrac{K_{as}}{K_{bs}}$. That is, the magnitude of $\dfrac{K_{as}}{K_{bs}}$ determines whether or not a given acid and a given base will react extensively in the given solvent to furnish a stable salt without what corresponds to hydrolysis in aqueous solution.

K_{as} is a measure of the extent to which the solvent tends to appropriate the proton of HA; while K_{bs} is a measure of the extent to which the solvent tends to appropriate the proton of BH^+. If K_{as} is much larger than K_{bs}, the cation, BH^+ can form.

Thus Hall and Conant (1928) (see figure 96) show that urea and other bases, which are too "weak" to form stable salts in water solution, can be titrated and form stable salts with sulfuric acid or perchloric acid in glacial acetic acid solution.
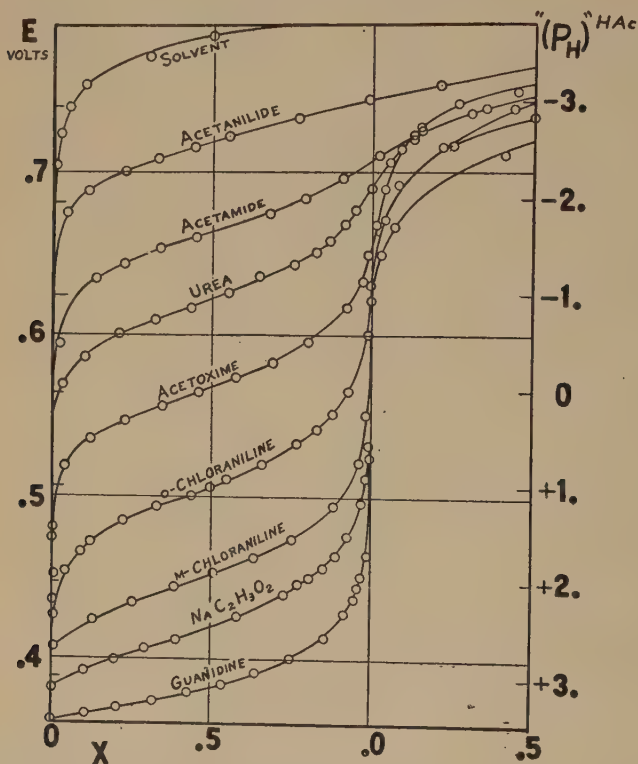
FIG. 96. TITRATION OF 0.05 N BASES IN GLACIAL ACETIC ACID WITH X EQUIVALENTS OF PERCHLORIC ACID

(Advance data furnished by courtesy of Dr. Norris F. Hall)

In liquid ammonia we have a solvent with a great "affinity" for hydrions. In this case the solvated hydrion is the ammonium ion NH_4^+. Franklin (1924) shows that phenolphthalein in liquid ammonia is colorless but on addition of potassium amid the red color develops.

$$KNH_2 + HP \rightarrow KNH_3^+ + \qquad P-$$
$$\text{colored anion}$$
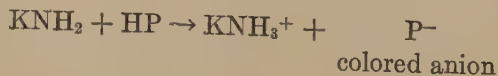
On "back-titration" with the acid, $(NC)_2NH$, we may regard this acid to furnish hydrions which are solvated to NH_4^+. H^+ $+ NH_3 = NH_4^+$. This ammonium ion, solvated proton, reacts as follows

$$NH_4^+ + P^- = NH_3 + HP$$
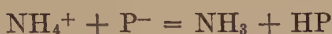
Thus the discharge of color in a liquid ammonia solution of phenolphthalein *salt* may be attributed to the *acidifying* effect of the *ammonium ion!*

In their study of glacial acetic acid solutions Hall and Conant (1927) and Conant and Hall (1927) use the cell

$$
\text{Pt} \left| \begin{array}{l} C_6Cl_4O_2 \text{ (sat.)} \\ C_6Cl_4O_2H_2 \text{ (sat.)} \\ \\ \text{HX in glacial} \\ \text{acetic acid} \end{array} \right| \text{Bridge} \left| \begin{array}{l} \text{KCl, (sat.)} \\ \text{HgCl} \\ \\ \text{aqueous} \end{array} \right| \text{Hg}
$$
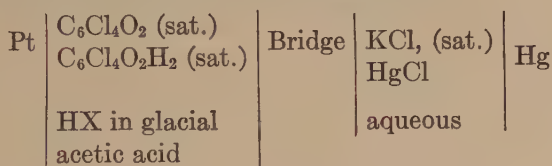
For a note on the chloranil electrode see page 417.

The bridge was a supersaturated solution of lithium chloride in acetic acid, crystallization being inhibited by a small amount of gelatin. This solution was enclosed in a glass-stoppered U-tube. Because of the high resistance of the cell, a quadrant electrometer was used as null-point instrument.

Figure 96 shows the results with several bases titrated with perchloric acid in glacial acetic acid. The ordinates are: on the left the potentials of the cell and on the right the "pH numbers"[3] calculated with an arbitrary reference point which is defined by

$$(\text{pH})_{HAc} = \frac{0.566 - \mathbf{E}}{0.0591} \text{ at } 25°.$$

[3] It will be noted that the description of the data shown in figure 96 can be accomplished by use of the potentials without the so-called pH values. In either case an assumption regarding the phase-boundary potential has been used. According to the temperament of the reader he will be pleased or offended by the use of "pH" in this instance. No fundamental objection can be raised since Conant and Hall state their assumptions and use pH in the activity sense. However, their values are such as to make correction factors several thousand times the quantity corrected *if* the connotation of a "corrected concentration" be retained for "the activity." If this connotation be retained, the use of "pH" in these cases is inartistic. Conant and Hall speak of super-acid solutions in these cases. Compare page 38.

TABLE 68

Indicators and buffers in glacial acetic acid

(After Conant and Hall (1927))

	POTENTIAL							
	756 millivolts	730 millivolts	686 millivolts	655 millivolts	625 millivolts	599 millivolts	566 millivolts	541 millivolts
A' Benzalacetophenone.........	pale yellow	colorless	colorless	colorless	colorless	colorless	colorless	colorless
B Triphenylcarbinol.........	yellow	pale yellow	pale yellow	colorless	colorless	colorless	colorless	colorless
C Diphenyl-α-naphthylcarbinol...	blue	blue	blue	colorless	colorless	colorless	colorless	colorless
D' Piperonalacetophenone.........	orange	yellow	yellow	pale yellow	pale yellow	pale yellow	pale yellow	pale yellow
E Dianisylcarbinol.........	orange	salmon	salmon	pale salmon	colorless	colorless	colorless	colorless
F' Anisalcinnamalacetone.........	carmine	red	red	orange	orange	orange yellow	yellow	yellow
G' Dipiperonal-acetone.........	purple	red	red	salmon	orange	yellow	pale yellow	pale yellow
H' Dianisalacetone.........	pink	red	red	red	red	orange	yellow	pale yellow
I Diphenylanisyl carbinol.........	brown orange	brown orange	brown orange	orange	orange	yellow orange	yellow	pale yellow
J Phenylxanthydrol.........	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Buffer number.........	1	2	3	4	5	6	7	8
Buffer composition.........	0.1 M H₂SO₄	0.064 M H₂SO₄	Acetanilid 0.76 neut.	Benzamid 0.4 neut.	Acetanilid 0.55 neut.	Urea 0.75 neut.	Urea 0.44 neut.	Urea 0.14 neut.
"pH".........	-3.22	-2.78	-2.03	-1.5	-1.0	-0.55	0.0	+0.42

On this scale the zero for pH is the value of a urea solution 44 per cent neutralized.

In table 68 are shown buffer solutions in glacial acetic acid prepared from sulfuric acid (nos. 1 and 2) from acetanilid and sulfuric acid (no. 3) from benzamid and sulfuric acid (no. 4), from acetanilid and sulfuric acid (no. 5) and from urea and sulfuric acid (nos. 6, 7 and 8). The potentials of the above cell are shown in the upper row of the table and the "pH" value in the lowest row. The color changes of several indicators in these buffer solutions are indicated in the table.

Bishop, Kittredge and Hildebrand (1922) used the following cell for titrations in ethanol.

$$\text{H}_2 \text{ (1 atmos.), Pt} \left| \begin{array}{c} \text{Solution in} \\ \text{Ethanol} \end{array} \right| \begin{array}{c} \text{NaBr (0.1 N)} \\ \text{Ethanol} \end{array}, \text{ HgBr} \left| \text{Hg} \right.$$
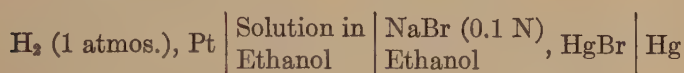
They titrated various acids with a solution of sodium ethylate and various bases with anhydrous HCl dissolved in ethanol.

Bishop, Kittredge and Hildebrand determined roughly the positions of color-change of various indicators on an arbitrary scale.

Michaelis and Mizutani (1925) report upon the changes of apparent dissociation constants (expressed as pK') of several acids, of ammonia and of several ampholytes as the solvent is gradually changed from aqueous to alcoholic through intermediate mixtures. While a rough parallelism is to be noticed in the changes of pK for certain acids, there remain notable exceptions. Michaelis and Mizutani (1924) give the changes in apparent pK' of nitrophenol indicators and phenolphthalein with change in the alcohol content of the solution. See also Kolthoff (1923), Thiel, Wülfken and Dassler (1924).

Cray and Westrip (1925) have calibrated a series of buffer solutions and worked out the "pH-ranges" of various indicators for acetone containing 10 volumes of water in 100 volumes of acetone-water.

Linderstrøm-Lang (1927) discusses the advantages of titrating amino acids in acetone solution.

For an example of a study of equilibria in two phase systems see Murray (1923).

The quinhydrone electrode has been used in the study of non-aqueous solutions by Schreiner (1924), Larrson (1924), Ebert (1925), Millet (1927), Pring (1925), Cray and Westrip (1925), Lund (1926).

A review of the electrochemistry of non-aqueous solutions is given by Walden (1924) and Müller (1924). See also Germann (1925).

CHAPTER XXX

APPLICATIONS

Finally, acidity and alkalinity surpass all other conditions, even temperature and concentration of reacting substances, in the influence which they exert upon many chemical processes.—L. J. HENDERSON.

GENERAL REMARKS

It is because of the great variety of applications in research, routine and industry that the theories and devices outlined in the previous chapters have been developed. The physical chemist sees in them the instruments of approximation or of precision with which there have been discovered orderly relations of inestimable service to the chemist and with which there have been established quantitative values for free energy changes. The biochemist might almost claim some of these methods as his own, not only because necessity has driven him to take a leading part in their development, but also because their application has become part of his daily routine in very many instances.

As a comprehensive generalization it may be said that the hydrogen ion concentration of a solution influences in some degree every substance with acidic or basic properties. When we have said this we have said that the hydrogen ion concentration influences the great majority of compounds, especially those of biochemical interest. Such a generalization, however, would be misleading if not tempered by a proper appreciation of proportion. Rarely is it necessary to consider the ionization of the sugars since their dissociation constants are of the order of 10^{-13} and their ionization may usually be neglected in the pH region encountered in physiological studies. Likewise there are zones of pH within which any given acidic or basic group will be found in dilute solution to be in a practically undissociated or fully dissociated state. Perhaps there is no more vivid way of illustrating this than by a contemplation of the conduct of indicators. Above a certain zone of hydrogen ion concentration phenol-

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phthalein solutions are colorless.   Below this zone (until intense alkalinity is reached) only the colored form exists.   Within the zone the color of a phenolphthalein solution is intimately related to the hydrogen ion concentration.   The conduct of phenolphthalein, which happens to be visible because of tautomeric changes which accompany dissociation, is a prototype of the conduct of all acids.   Just as we may suppress the dissociation of phenolphthalein by raising the hydrogen ion concentration of the solution so may we suppress the dissociation of any acid if we can find a more intensely ionizing acid with which to increase the hydrogen ion concentration of the solution.   Similar relations hold for bases, and, if we regard methyl red as a base, we may illustrate with it the conduct of a base as we illustrated the conduct of an acid by means of phenolphthalein.

Such illustrations may serve to emphasize the reason underlying the following conclusion.   Whenever, in the study of a physiological process, of a step in analysis requiring pH adjustments or of any case involving equilibria comparable with those mentioned above, there is sought the effect of the pH of the solution, it may be expected that no particularly profound effect will be observed beyond a certain zone of pH.   Within or at the borders of such a zone the larger effects will be observed.   From this we may conclude that the methods of determining hydrogen ion concentrations should meet two classes of requirements.   In the first place, when the phenomenon under investigation or control involves an equilibrium which is seriously affected by the pH of the solution, the method of determining pH values should be the most accurate available.   In the second place, when the equilibrium is held practically constant over a wide range of pH, an approximate determination of pH is sufficient and refinement may be only a waste of time.

Neglecting certain considerations which often have to enter into a choice of methods it may be said that the electrometric method had best be applied in the first case and the indicator method in the second.   When the nature of the process is not known, and it therefore becomes impossible to tell *a priori* which method is to be chosen, the colorimetric method becomes a means of exploration and the electrometric method a means of confirmation.

Exception will be taken to this statement as comprehensive for there are cases where one or another method has to be discarded because of the nature of the solution under examination. Nevertheless, in general, the utility of the colorimetric method lies in its availability where approximations are needed and exact determinations are useless and also in its value for reconnaissance; while the value of the electrometric method lies in its relative precision.

In some instances the qualitative and quantitative relations of a phenomenon to pH should be carefully distinguished. Note, for instance, the significance of an optimum or characterizing point. Consider the conduct of phenol red and of cresol red. These two indicators appear to a casual observer to be very much alike in color and each exhibits a similar color in buffer solutions of pH 7.6, 7.8, etc. Careful study, however, shows that each point on the dissociation curve of phenol red lies at a lower pH than the corresponding point on the dissociation curve of cresol red. If the half transformation point be taken as characteristic it may be used *to identify* these two indicators. Likewise it is the *dissociation constant* of an acid or a base, the *isoelectric point* of a protein, the *optimum pH* for acid agglutination of bacteria, or an optimum for a process such as enzyme activity that furnishes *characteristic* data.

When there is observed a correlation between pH and some effect, the mere determination of pH alone will of course throw but little light upon the real nature of the phenomenon except in rare instances. Determination of the hydrogen ion concentration will not even distinguish whether a given effect is influenced by the hydrogen or the hydroxyl ions, nor will it always reveal whether the influence observed is direct or indirect. The so-called hydrion concentration or pH number of a solution may be only an index of the position of an equilibrium state in which the hydrion is an entity of no great importance from a physical point of view. See Chapter XXVII. However, if only as an index, its importance remains. Therefore advantage should be taken of the comparative ease with which the concentration of hydrogen ions may be determined or controlled and its influence known or made a constant during the study of any other factor which may influence a process. From this point of view methods of deter-

mining hydrogen ion concentration take their place beside ther-
mometers, buffer mixtures beside thermostats and automatic
control devices beside thermoregulators.

Indeed it may be said that the failure to take advantage of
these devices is still a prolific source of error in the experimental
work of every branch of science having to do with solutions.   In
one case the neglect may be gross; in another case it may be a
perfectly excusable misjudgment.   A complete understanding of
the effects of the hydrogen or hydroxyl ion, or of the effects of
those equilibrium states of which pH is an index, is very far from
attainment and those who faithfully control their solutions are
often rewarded by the most surprising results.   To emphasize
this aspect we may call attention to the fact that while the disso-
ciation of glucose is negligible in the region of pH 7 so far as any
great effect upon the displacement of other acid-base equilibria
is concerned, a converse effect, which does not belong to the
category of equilibria, is decidedly not negligible.   A shift in pH
from 7.0 to 7.4 has a very marked influence upon the conduct of
glucose in heated solutions as every one who has made culture
media knows.

Nor is it adequately realized that the formulations of the
measurements we make are so fundamentally thermodynamic
that they may ignore intermediate stages in chemical trans-
formations or may lead to false impressions regarding the entities
which convenience forces us to symbolize in some particular way.
Reference was made on page 540 to the fact that for the purposes
of a limited thermodynamic treatment it is a matter of indif-
ference whether we regard the hydrion in aqueous solution to be
hydrated or not. Yet this item may leap into importance when
we attempt to compare events in different solvents.   So, also, the
ignoring of groups which, as measured by ordinary methods,
appear to have in aqueous solution little tendency to dissociate,
may obscure their parts in kinetic events.

Our methods of formulation tend to emphasize either one
particular function or some refinement of this function that re-
quires a new symbolism. We may then fall victim to that
restraint upon outlook which led Comte to remark: "every
attempt to employ mathematical methods in the study of chem-
ical questions must be considered profoundly irrational and con-

trary to the spirit of chemistry. . . . ." Mellor, who gives this translation of Comte, believes that the key to these remarks is Comte's statement that "our feeble minds can no longer trace the logical consequences of the laws of natural phenomena whenever we attempt to simultaneously include more than two or three essential factors." Nevertheless the requirements of biochemistry impose the task of simultaneously including *many* factors. If this task is to be met, the physical chemist must develop methods of formulation of such fundamental directness, simplicity and generality that the biochemist will not mistake the formalities of convenience which lead to "vanishing particulars" for those other and still necessarily artificial devices of the intellect which lead to a comprehension of togetherness.

ON THE BIBLIOGRAPHY

As mentioned in the first edition of this book, the applications had, by 1920, become so numerous, and in many instances so detailed, that the time had come for a redispersion among the several sciences of the material that had from time to time been assembled by authors who were intent upon emphasizing the importance of hydrion concentration. The crude statistics noted in the preface to this, the third edition, indicate the appalling task that awaits any one who attempts to assemble a complete bibliography. Even the limited comprehensiveness of the bibliography of the second edition is no longer practicable. Consequently, while this chapter retains its old form, there has had to enter the element of selection. This has been distressing to the author, ostensibly because of the injustices that may be done to subject matter and to leading authors, but probably because selection reveals the ignorance of the selector. However, for those students who desire "leads" in their first attack upon the literature there may remain some value in the following sketches.

These sketches and various assemblies of references in the text serve as crude indices to the bibliography. In this are to be found only some six hundred of the references in the second edition. Consequently the older edition should be consulted for many of the earlier references. The following selection of over 1600 references is not to be considered in any other way than as an *introduction to* a vast literature.

GENERAL TREATISES

What may be called the fundamental classic is the paper published by S. Arrhenius in 1887. The subsequent evolution of the theory of electrolytic dissociation to 1914 is reviewed by Arrhenius (1914) and in Faraday Society Symposium (1927).

Among several papers of historical interest is that of Bugarzsky and Liebermann (1898) who first applied the hydrogen electrode to a biochemical problem, and Böttger's paper on titration.

Two classics of biochemistry are Sørensen's (1909) *Études enzymatiques II* in which are organized the subjects of buffer solutions and indicators and Henderson's (1909) *Das Gleichgewicht zwischen Basen and Säuren im tierischen Organismus* in which is outlined the acid-base equilibria of the blood.

The papers of Noyes (1910) and of Bjerrum (1914) on the theory of titration have needed but slight elaboration since their publication.

No one has contributed so widely to the applications of indicator and electrode methods as has Michaelis. Indeed an excellent cross-sectional view of the variety of these applications can be obtained by reading Michaelis' numerous papers. These are easily traced in abstract journals and will not be cited in detail. The first edition (1914) of Michaelis' *Die Wasserstoffionenkonzentration* contained brief reviews of applications. The second edition (1922), now in an English translation by Perlzweig (1926), elaborated the theoretical sections of the first.

As the subject has gained prominence in special fields the journals and compilations covering these fields have published reviews. These reviews are too numerous to mention. Books by the following authors may be cited:

Kolthoff (1923). *Der Gebrauch von Farbenindicatoren.* Springer, Berlin. French edition translated by Vellinger, 1927. English edition translated by Furman (1926). John Wiley.

Kopacewski (1926). *Les ions d'hydrogène. Signification, mesure, applications, données numériques.* Gauthier-Villars, Paris.

Michaelis (1914–1923). *Die Wasserstoffionenkonzentration.* Springer, Berlin. The second edition (1923) enlarged upon only the theoretical part of the first. Second edition translated into English by Perlzweig, 1926. Williams and Wilkins, Baltimore.

Mislowitzer (1928). *Die Bestimmung der Wasserstoffionenkonzentration von Flüssigkeiten.* Springer, Berlin.

L. Michaelis

Mizutani (1925). *The determination of hydrogen ions.* (In Japanese) Tokyo.

Prideaux (1917). *The theory and use of indicators.* Van Nostrand, N. Y.

Vincent (1924). *La concentration en ions hydrogène et sa mesure par la méthode électrométrique.* Hermann, Paris.

See also Rona (1926).

SPECIAL APPLICATIONS

Analyses. Hydrion methods have manifold applications through the theory of titration. See Chapter XXVIII. Intimately related are methods of oxidation-reduction titration, one aspect of which was discussed in Chapter XVIII. For particulars in regard to potentiometric titrations in analysis see Müller (1926), Kolthoff and Furman (1926) and Popoff (1927). The empiricism that characterized the older developments in analytical chemistry often left specifications for the use of mixtures of acids and their salts. These we now know control the ratios of the concentrations of ions and undissociated molecules, and a useful index to such a ratio is the proper combination of the pH number of the solution and the pK_a or pK_b number of a given system. The older specifications also left directions for delicate proportionment of reagents which often can be conveniently expressed in terms of pH. These conveniences are coming into wide use without that systematic record which permits adequate references. As examples in the field of inorganic analysis there may be cited the papers by Blum (1913, 1914 and 1916), Fales and Ware (1919), Hildebrand and coworkers (1913–1916), Robinson (1923). Among several methods of biochemistry there may be mentioned the benzidine sulfate method for the determination of sulfate (see any text). General principles of the application are to be found in modern texts of inorganic analysis, e.g., Kolthoff and Menzel's *Massanalyse* (1928), Fales (1925), and the older text of Stieglitz (1917). Separations of proteins, amino acids etc. involve constant attention to pH. See, for example, Abel *et al.* (1927), Vickery and Leavenworth (1927), Foster and Schmidt (1923).

Bacteriology. The applications in bacteriology up to 1917 are reviewed by Clark and Lubs (1917). For a bibliography on the rôle of ions in general in bacterial physiology see I. S. Falk (1923). For various modern applications see Jordan and Falk (1928), Buchanan and Fulmer (1928).

Acid agglutination of bacteria, first definitely recognized by Michaelis (1911) in its relation to hydrion concentration has been found to be of some diagnostic use. For example, Gillespie (1914). Eisenberg gives an extensive bibliography up to 1919. See especially Northrop and DeKruif (1922) and De Kruif (1922).

Adjustment of the reaction of media by the old titrimetric procedure was criticized by Clark (1915), and, on the introduction of suitable indicators and the evidence for the advantage of adjusting on the pH basis, the titrimetric method has been abandoned for more significant and easier modern methods. Studies on growth optima (which see below) have shown

that for the cultivation of most saprophytes approximate indicator control is sufficient. For particular purposes and especially for the study of certain important pathogens, it is well to adjust with the precision attained with standards. Seldom is electrometric control necessary. Data for special media and special organisms now usually accompany all descriptions. See, for example, *Standard Methods of Water Analysis*, H. N. Cohn (1919), Medical Research Committee (1919).

Antigenic action. For example see Falk and Powdermaker (1925). See *Immunology*.

Bacterial products, purification. For example, see Michaelis and Davidsohn (1924).

Bacteriophage. For examples see, Davison (1922), Arloing and Chavanne (1925), and Todd (1927).

Bacteriostatic action of dyes. For examples see, Churchman (1922), Smith (1922), and Stearn and Stearn (1924, 1926).

Disinfectant action of acids and bases is certainly in large measure a function of hydrogen and hydroxyl ion activity; but specific effects of certain acids and bases which were suspected before, have now been more clearly demonstrated by the use of hydrogen ion methods. By the conductivity method, Winslow and Lochridge (1906) were able to show the effect of the hydrogen ion in simple solutions and predicted relations which more powerful methods have extended to complex media. Cohen (1922) has reviewed certain of the fundamental relations between pH and viability of bacteria under sublethal conditions. The more direct action of hydrion concentration upon cells must be distinguished from its control upon the effective state of a toxic compound. Knowledge of pH effects is therefore essential to the assay of disinfectants and to the advancement of chemotherapy.

See review by Bonacorsi (1923), and references by Jarisch (1926). Examples: Michaelis and Dernby (1922), Dernby and Davide (1922), Eggerth (1926), Fleischer and Amster (1923), Kuroda (1926), Levine, Toulouse and Buchanan (1928).

Electrophoresis. Winslow, Falk and Caulfield (1923), and papers by Falk in *Journal of Infectious Diseases*, 1925–1927.

Gram reaction. See "Staining."

Influence of pH on bacterial metabolism. The reaction of the medium, even within the zone of optimal bacterial growth, is found to influence either the absolute rate, or the relative rate of specific types of metabolism. Not only the activity but also the production of enzymes is influenced; and the production of special products such as toxins is partially controlled by the pH of the medium.

Examples: Virtanen and Bärlund (1926), Arzberger, Peterson and Fred (1920), Clark (1920), Avery and Cullen (1920), Merrill and Clark (1928).

Morphology. Example: Reed and Orr (1923).

Motility. Example: Reed and MacLeod (1924).

Optimal Zones and the limits of growth and general metabolism have naturally been the chief interest in the first surveys of the influence of hy-

TABLE 69

Optimum and limiting reactions for the activities of microörganisms
(After Waksman, 1927)

ORGANISMS	ACID MAXIMUM	OPTIMUM	ALKALI MAXIMUM	AUTHOR
	pH	*pH*	*pH*	
Nitrosomonas............	3.9	7.7–7.9	9.7	Gaarder and Hagen
Nitrobacter.............	3.9	6.8–7.3	13.0	Meek and Lipman
Nitrification in soils.....	3.5	6.5–7.5	11.9	Gerretsen, Waksman
Thiobacillus denitrificans	5.0	7.0–9.0	10.75	Trautwein
Th. thiooxidans..........	1.0	2.0–4.0	6.0(?)	Waksman and Starkey
Bac. pycnoticus..........	5.2	6.8–8.7	9.2	Ruhland
Bac. amylobacter........	5.7	6.9–7.3		Dorner
Azotobacter..............	5.6–6.0	6.5–7.8	8.8–9.2	Gainey, Johnson and Lipman, Yamagato Itano, Stapp
Bact. radicicola of:				
Medicago and Melilotus................	5.0			
Pisum and Vicia......	4.8			
Trifolium and Phaseolus................	4.3		11.0	Fred and Davenport, Fred and Loomis, Bryan
Soja.................	3.4			
Lupinus..............	3.2			
Bact. coli..............	4.4	6.5	7.8	Dernby
Bact. vulgare...........	4.4	6.5	8.4	Dernby
Bact. pyocyaneum.......	5.6	6.8	8.0	Dernby
Bact. stutzeri...........	6.1	7.0–8.2	9.6–9.8	Zacharowa
Bac. subtilis.............	4.2	7.5–8.5	9.4	Itano
Bac. putrificus..........	5.8	5.8	8.5	Dernby
Act. scabies.............	4.8–5.0	6.5–7.5	8.7	Gillespie, Waksman
Mucor glomerula........	3.2–3.4		8.7– 9.2	Johnson
Asp. terricola...........	1.6–1.8		9.0– 9.3	
Pen. italicum...........	1.6–1.8		9.1– 9.3	
Fus. oxysporum.........	1.8–2.0		9.2–11.1	
Asp. niger..............	1.2	1.7–7.7		Terroine and Wurmser
Gibberella saubinetii.....	3.0	4.8–9.4	11.7	MacInnes
Spore germination of fungi.................	1.5–2.5	3.0–4.0		Webb

For other data on the culture of microörganisms other than bacteria see Sakamura (1924), A. Saunders (1924), Sartory, Sartory and Meyer (1927), Scott (1924), Waksman (1927), Webb and Fellows (1926).

drion concentration upon bacterial activity. It is now clear that more exact studies will have to differentiate between optimal pH to initiate growth, optimal zones of growth, optimal zones for general or special metabolism, optimal zones for preservation, etc. The self-limitation first clearly defined by Michaelis and Marcora (1912) has been applied to certain practical tests, for example see Clark (1915), Avery and Cullen (1919). pH limits for special organisms of commercial significance are exemplified by control of "rope" in bread (Cohn, Wolbach, Henderson and Cathcart, 1918) and potato scab (Gillespie and Hurst, 1918). Growth optima and limits usually accompany modern descriptions and are best sought in the special literature. As illustrations there may be quoted table 69. Several of the pH numbers are first approximations.

Sporulation. Example: Itano and Neill (1919).

Testing fermentation. See, for examples: Chesney (1922), Clark and Lubs (1917), Nichols and Wood (1922).

Toxin production. Examples: Abt and Loiseau (1922), Davide and Dernby (1921), Dernby and Allander (1921), Dernby and Walbum (1923), Jonesco-Mihaesti and Popesco (1922), Walbum (1922–1923), Cook *et al.* (1921). See also *Immunology.*

Vaccine virus. Defries and McKinnon (1926).

Virulence. Felton and Dougherty (1924), Defries and McKinnon (1926).

Viscosity of bacterial suspensions. Falk and Harrison (1926).

Blood. The hydrion concentration, or the *ratio* between acid residues and their anions, is, with the exception of temporary fluctuations (exercise, etc.), regulated with remarkable constancy in the blood of any normal individual. It very seldom varies far from pH 7.4. Van Slyke (1921) places the normal variation between 7.3 and 7.5 and the limits usually compatible with life at about 7.0 and 7.8, although he takes these as data convenient to a general description.

The bicarbonate-carbonic acid equilibrium is important because one of the chief functions of the blood is to carry CO_2. The bicarbonate system is also used as an indicator.

See *carbonate equilibria* for the derivation of

$$pH = pK_1' + \log \frac{[HCO_3^-]}{[\text{free } CO_2]}$$

and

$$[\text{free } CO_2] = K_oP$$

Inspection of relations involving the carbonate ion, CO_3^{--} (see page 561), will show that, at pH 7.4, $[CO_3^{--}]$ may be neglected and that the fixed carbon dioxide may be regarded for present purposes as almost entirely in the form of bicarbonate. Therefore the above equations suffice. They can be combined to

$$pH = pK_1' + \log \frac{[HCO_3^-]}{K_oP}$$

If equations in terms of activities are to be used, it is convenient to know that Van Slyke, Hastings, Murray and Sendroy (1925) have estimated the ionic strength of blood to be $\mu = 0.16$.

In using the ideal equation with whole blood, serum or solutions such as hemoglobin, the constants must be evaluated for the specific conditions. Van Slyke, Cullen and Hastings (1922) use the values shown below

SOLUTION	K_o WHEN FORMULA IS USED FOR MILLIMOLS	K_o WHEN FORMULA IS USED FOR VOLUME—PER CENT	pK_1'
Water.............................	0.0326	0.0730	
Serum or plasma..................	0.0318	0.0712	6.14
Whole blood......................	0.0300	0.0672	6.18
12 per cent Hemoglobin in 30 mM NaHCO₃.......................	0.0312	0.0699	6.18

Since $[HCO_3^-] = [\text{Total } CO_2] - [\text{free } CO_2]$, the above equation may be used in the form

$$pH = pK_1' + \log \frac{[\text{Total } CO_2] - K_oP}{K_oP}$$

This shows that, for the definition of the equilibrium state, two measurements are necessary: pH and $[\text{Total } CO_2]$; pH and P; or $[\text{Total } CO_2]$ and P.

Fifty volumes per cent total CO_2 and pH 7.4 may be regarded as an orienting norm.

Investigative methods utilize pairs of these quantities in determining, among other constituents of the blood, ratios of acid residues to anions, on the principle that, at a common pH value, the determination of $\dfrac{[HCO_3^-]}{[\text{free } CO_2]}$ measures all such ratios of any anion concentration to the concentration of the dissociation residue.

A tentative *hypothesis* which is useful for a gross description of the manner in which these ratios is kept constant is that the "respiratory center" is sensitive to changes of pH, stimulating lung-ventilation as pH decreases, and checking lung-ventilation as pH increases. This hypothesis is disputed. (See for example Y. Henderson, 1922.) It remains a hint the value of which is lost when it is forgotten that hydrion concentration of itself, when unrelated to definite equilibria, means little *chemically.*

When "combustion" in the tissues is incomplete and acid products of combustion replace the CO_2 which the lungs can eliminate, and when these non-volatile or "fixed" acids cannot be eliminated by the kidneys as fast as produced, the fixed acid anions will replace bicarbonate ions. Hence $[\text{Total } CO_2]$ in the last equation has a significance of its own.

While the bicarbonate system is important in itself, it is not the chief buffer system of the blood. The protein systems are the more powerful buffers and of these the systems involving hemoglobin and oxyhemoglobin are the most important. Here are met two distinct aspects. In the first place oxyhemoglobin behaves in a way conveniently described as if it were a stronger acid than hemoglobin. Consequently oxidation in the lungs results in the virtual transfer of base from bicarbonate to oxyhemoglobin tending to displacement of CO_2. In the tissues the reverse effect, attending reduction of the blood pigment, provides base to combine isohydrically with CO_2. In addition, both hemoglobin oxyhemoglobin, and the other proteins exercise ordinary buffer action. In these two senses the blood pigment is the most important carrier of CO_2 as well as the chief carrier of oxygen.

The buffers of the blood are distributed between the cells and plasma. Not all the constituents of the buffer systems diffuse freely between the cells and plasma. Of those constituents of the cell, which are of chief importance and which do not diffuse out, are the several forms of hemoglobin and oxyhemoglobin and the base K^+. Likewise the plasma proteins and Na^+ do not diffuse inward. There is established a complex Donnan equilibrium (see page 568) in the maintenance of which, during CO_2 exchanges, the anions HCO_3^- and Cl^- migrate in and out to adjust electroneutrality, and water migrates in and out to maintain osmotic equilibrium.

Intimately connected with the regulation of the hydrogen ion concentration of the blood are the functions of the kidneys. [See Cushny (1926), and Marshall (1926).] By their action there are eliminated the non-volatile products of metabolism, several of which are of great importance for the acid-base equilibria of the blood. The colorimetric determination of the pH of the urine is a comparatively simple procedure which furnishes valuable data when properly connected with other data. (See for instance Blatherwick, and the works of Henderson, of Palmer, of Van Slyke, of Cullen, of Hastings, of Austin, etc.)

While the greatest interest has centered in the subjects briefly mentioned above, there remain innumerable other problems of importance. Of these there may be mentioned the relation of the pH of the blood to the calcium-carrying power, to the activity of various enzymes, to the permeabilities of tissue membranes, to the activity of leucocytes, and to various reactions used in the serum diagnosis of disease.

There have been numerous studies of the blood of lower animals. See for example, Bodine (1926), Duval (1924), Glazer (1925), Gellhorn (1927), Hawkins (1924), and references in Porter (1927).

Gasometric, colorimetric and potentiometric methods of determining pH numbers of blood, serum etc. are so highly specialized that the special literature of the technique and of the principles of the equilibria concerned should be consulted.

The following references are selected from a huge literature as being especially helpful.

Historical. Henderson (1908–1909).

Reviews and theoretical discussions. Austin and Cullen (1926), Henderson (1926), Murray and Hastings (1925), Van Slyke and Van Slyke *et al.* (1921–1927), Warburg (1922).

Methods. Austin, Stadie and Robinson (1925), Cullen (1922), Cullen and Hastings (1922), Cullen, Keeler and Robinson (1925), Dale and Evans (1920), Eisenman (1927), Hastings and Sendroy (1924–1925).

Physiological data. Cullen and Robinson (1923), Drury, Beattie and Rous (1927), Gamble (1922).

Respiration. Haldane (1922), Barcroft (1925).

Carbonate equilibria. Because of their general importance to biochemistry and general chemistry, equilibria in carbonate and bicarbonate solutions deserve special mention. The following treatment is necessarily brief.

When carbon dioxide dissolves in water it presumably is present both as anhydrous CO_2 and as the hydrate H_2CO_3, carbonic acid. For a discussion of the rate of hydration and proportions of the forms, see experiments and references by Buytendijk, Brinkman and Mook (1927).[*] Analytical methods do not ordinarily distinguish the two forms, and, since the sum of the two is generally the more important quantity, we may write the equilibrium equation for the relation between a partial pressure, P (atmospheres) of gaseous carbon dioxid and the dissolved carbon dioxide as follows:

$$[CO_2] + [H_2CO_3] = [\text{free } CO_2] = K_o'P \tag{a}$$

In the presence of bases we still have the above relation holding between the partial pressure and that portion of the total CO_2 which remains uncombined. However, variation in the composition of the solution will vary the magnitude of K_o. Dissolved CO_2 reacts with water and since $[H_2O]$ may be regarded as constant we have the equilibrium equation

$$\frac{[CO_2]}{[H_2CO_3]} = K'' \text{ or } \frac{[CO_2] + [H_2CO_3]}{[H_2CO_3]} = K'' + 1 \tag{b}$$

The H_2CO_3 dissociates in steps and for the first step the equilibrium condition is:

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = K''' \tag{c}$$

Combining equations (b) and (c) and collecting constants we have

$$\frac{[H^+]\,[HCO_3^-]}{[CO_2] + [H_2CO_3]} = K_1'$$

or using the convention mentioned above

$$\frac{[H^+]\,[HCO_3^-]}{[\text{free } CO_2]} = K_1' \tag{d}$$

---

[*] Cf. Faurholt (1924).

The constant K_1' is sometimes called the first dissociation constant of carbonic acid. It is not strictly so but is rather of the nature of an "apparent dissociation constant." K_1' is more useful than the true dissociation constant but is probably much smaller.

For the second stage of dissociation the equilibrium condition is:

$$\frac{[H^+]\ [CO_3^{--}]}{[HCO_3^-]} = K_2' \tag{e}$$

For simplicity the above equations were stated in terms of concentrations, as is permissible for ideal conditions, for a limited range of conditions or for limiting equations. Equations (a), (d) and (e) may now be restated with correction terms or with activities.

$$[\text{free } CO_2]\gamma_0 = (\text{free } CO_2) = K_0 P \tag{f}$$

$$\frac{(H^+)\ [HCO_3^-]\ \gamma_1}{(\text{free } CO_2)} = \frac{(H^+)\ (HCO_3^-)}{(\text{free } CO_2)} = K_1 \tag{g}$$

$$\frac{(H^+)\ [CO_3^{--}]\ \gamma_2}{(HCO_3)} = \frac{(H^+)\ (CO_3^{--})}{(HCO_3^-)} = K_2 \tag{h}$$

The relation

$$[\text{free } CO_2] = \frac{K_0}{\gamma_0} P$$

may be assumed to be subject to use with solutions containing no free base which would form appreciable amounts of bicarbonate and carbonate ions. Values of $\dfrac{K_0}{\gamma_0}$ for solutions of sodium chloride are given by Johnston (1915) from the data of Bohr.

Concentration of
NaCl, molar... 0.0   0.1   0.2   0.3   0.5   1.0
$\dfrac{K_0}{\gamma_0}$ at 25°....... 0.0338 0.0329 0.0321 0.0314 0.0300 0.0270

See also Walker, Bray and Johnston (1927).

Randall and Failey (1927) tabulate values of γ_0 at 15° and 25° for various ionic strengths, using, however, *molality* as the basis of calculation. Their equation is

$$\text{Molality of } CO_2 = \frac{KP}{\gamma}$$

In water the solubility of CO_2 is 0.0478 molal at 15° and 0.0370 molal at 25°. Representative values of γ at 25° are:

SALT	μ	γ
KCl.................... {	0.508	1.072
	1.031	1.143
HCl.................. {	0.505	1.015
	2.080	0.998

See also section on "Blood," and papers by Van Slyke and Neill (1924) and Van Slyke and Sendroy (1927) for details of manometric measurement of CO_2 extracted from solutions.

TABLE 70

Values of log φ interpolated at a series of ionic strengths

(After Walker, Bray and Johnston, 1927)

μ	25° BASE			37° BASE			$\varphi25/\varphi37$
	K	Na	Li	K	Na	Li	
0.00	2.491	2.491	2.491	2.296	2.292	2.296	1.57
0.01	2.403	2.400	2.396	2.205	2.204	2.200	1.57
0.02	2.376	2.371	2.362	2.177	2.174	2.165	1.58
0.04	2.342	2.334	2.318	2.142	2.135	2.118	1.59
0.06	2.319	2.308	2.286	2.118	2.106	2.084	1.59
0.08	2.300	2.286	2.260	2.096	2.082	2.055	1.60
0.10	2.286	2.267	2.238	2.079	2.060	2.031	1.61
0.20	2.236	2.194	2.160	2.015	1.980	1.952	1.64
0.40	2.186	2.100				1.871	
0.60	2.158	2.034				1.828	
0.80	2.139	1.982					
1.0	2.122	1.939					
1.5	2.098	1.860					
2.0	2.085	1.802					
2.5	2.074	1.753					

Combination of equations (f) and (g) gives

$$\text{pH} - \log [HCO_3^-] + \log K_0 P = p\bar{K}_1 + \log \gamma_1 \qquad (i)$$

The quantities on the left are determinable if $[HCO_3^-]$ is regarded equal, for instance, to $[NaHCO_3]$.

Hastings and Sendroy (1925) find that pK_1 at 38° is 6.33 and $\log \gamma_1 = -0.5\sqrt{\mu}$. Hence, if we let $pK_1' = pK_1 + \log \gamma_1$

$$pK_1' = 6.33 - 0.5\sqrt{\mu}$$

Likewise they find at 38°C.

$$pK_2' = pK_2 + \log \gamma_2 = 10.22 - 1.1 \sqrt{}$$

By combining several activity coefficients and the first and second dissociation constants, Walker, Bray and Johnston (1927) derive:

$$\frac{[HCO_3^-]^2}{[CO_3^{--}]P} = \varphi$$

They tabulate the values of $\log \varphi$ at a series of ionic strengths and at 25° and 37°C.   See table 70.

"This table enables one to calculate the concentration of bicarbonate and of carbonate in any solution in equilibrium with the partial pressure P (atm.) of carbon dioxide, provided the total alkali associated with both carbonate and bicarbonate is known; or conversely, to compute the equilibrium pressure."
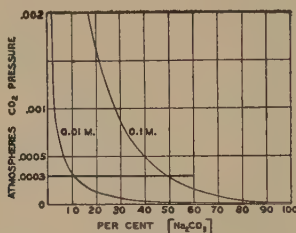
FIG. 97. RELATION OF PARTIAL PRESSURE OF CO₂ IN (ATMOSPHERES) TO PER CENT Na₂CO₃ IN CARBONATE-BICARBONATE MIXTURE

As an illustration there are given in figure 97 the pressures of CO_2 over a solution in one case 0.1 molal with respect to $[Na_2CO_3] + [NaHCO_3]$, and in the other case 0.01 molal with respect to the same sum, when the per cent of $[Na_2CO_3]$ is changed.   The CO_2 partial pressure of our atmosphere is about 0.0003 atmosphere.   The figure shows that the 0.01 M solution will absorb CO_2 when $[Na_2CO_3]$ is over 10 per cent while the 0.1 M solution will absorb CO_2 when $[Na_2CO_3]$ is over 50 per cent.

Equations (f), (g) and (h) give

$$(CO_3^{--}) = \frac{K_2 \, K_1 \, K_o \, P}{(H^+)^2}$$

The equilibrium for the dissociation of calcium carbonate is:

$$\frac{(CO_3^{--}) \, (Ca^{++})}{(CaCO_3)} = K$$

If ($CaCO_3$) is maintained constant by the presence of the solid phase

$$(CO_3^-) \, (Ca^{++}) = K_s$$

where K_s is the solubility product, or

$$(Ca^{++}) = \frac{K_s \, (H^+)^2}{K_o \, K_1 \, K_2 \, P}$$

Thus the activity (or concentration) of calcium in a solution in contact with $CaCO_3$ is a function of the hydrion activity and CO_2 partial pressure. This relation is of importance in geology as well as in biochemistry. See Hastings *et al.* (1927), and an application by Atkins (1922).

An interesting discussion of the importance of carbonate equilibria to life is given by Henderson in *The Fitness of the Environment*.

Catalysis. See Chapter XXVI.

Colloid chemistry. Sørensen, in the introduction to his 1917 paper, *Studies on Proteins*, discusses the significance to colloid chemistry of careful studies of acid-base equilibria in protein solutions. Michaelis, in *The Effects of Ions in Colloid Systems*, discusses several aspects, especially adsorption. Rideal (1926) gives brief treatments of many of the fundamental principles concerned.

There exists, in one school, a rather strange prejudice against attempts to make the methods of acid-base equilibrium studies yield what they are capable of yielding. This has doubtless been due in some measure to the disposition of another school to push the signal triumphs beyond clear accomplishment. The resulting confusion makes it impossible to give a fair statement even of the chief topics. The student will do well to cultivate ability to detect extremes of statement. He should know that innumerable investigators are proceeding, oblivious to controversies, to make the methods of hydrion control and measurement yield results of immediate practical and theoretical interest.

Reference to the rôle of hydrion concentration will be found in such general texts as those of: Freundlich (1922–1927), Bogue (1924), Colloid Symposium Monographs (1922–date).

Crystallization. In the crystallization of ampholytes, acids and bases, it is common practice to adjust the hydrion concentration of the solution to the point of incipient precipitation. See for instance the crystallization of egg albumin (Sørensen (1917) and of insulin (Abel, *et al.* (1927)).

Dr. Edgar T. Wherry calls my attention to the fact that it has long been known that the acidity of a solution may have some bearing on the habit of the crystals separating from it. Alum crystals are octahedral when deposited from strongly acid solutions, cubic when the acidity is reduced; sodium chloride is reported to show the reverse. (See Tertsch, 1926.) Thus far, however, only qualitative information is available, and the pH values at which habit-changes become significant remain to be determined. This may have technical bearings. See Saylor (1928).

Digestive system. The digestive tract is primarily the channel for the intense activity of hydrolytic enzymes and as such is provided with mechanisms for the establishment of hydrogen ion concentrations favorable to these enzymes. Hydrogen electrode methods have correlated the regional activity of particular enzymes with the reactions there found, have clarified some of the differences between the digestive processes of infancy and adult life, aided in attempts to explain the formation of acid and alkali and have been of service in the improvement of clinical methods for the assay of pepsin activity and the diagnosis of abnormal secretion of hydrochloric acid in the stomach. The control of specific physiological functions such as secretion of conditioning agents, permeabilities, and activities of the varied musculature, as well as investigations upon the condition in the digestive tract of substances such as calcium and phosphate are subjects which have been discussed. Shohl and King (1920) and Kahn and Stokes (1926) have reviewed and improved methods of studying gastric acidity. Some of the problems of gastric acidity have been reviewed by Michaelis (1927). Schwarz et al. (1924) and McClendon et al. have reviewed several aspects of digestion. For references on saliva see G. Clark and Carter (1927). As two of many examples of studies on lower animals see Yonge (1925), Redman et al. (1927).

Distribution coefficients. Imagine two phases in contact, e.g., water and benzene, and neglect the complexities due to the solubility of the substance of one phase in the other. Dissolve in either phase a substance A, and let it distribute itself between the two phases. Actually, or in imagination, let the substance A enter a vapor phase and assume Henry's law for the distribution between each of the solvents and the vapor phase where the partial pressure of A is P.

$$[A]_w = k_1 P \tag{a}$$

$$[A]_b = k_2 P \tag{b}$$

By (a) and (b)

$$\frac{[A]_w}{[A]_b} = \frac{k_1}{k_2} = K_d \tag{c}$$

The ratio $\frac{[A]_w}{[A]_b}$ should then be constant and independent of that concentration in either phase which is proportional to P. K_d is the so-called distribution coefficient.

Now let A be an acid, HA, and assume
1) Ionization in the water-phase

$$HA \rightleftharpoons H^+ + \overline{A}$$

2) The equilibrium

$$\frac{[H^+]_w \, [\overline{A}]_w}{[HA]_w} = K_a \tag{d}$$

3) The summation for the aqueous phase

$$[S]_w = [\overline{A}]_w + [HA]_w \tag{e}$$

4) The distribution of molecules.

$$\frac{[HA]_w}{[HA]_b} = K_d \tag{f}$$

Equations (d), (e) and (f) yield (g)

$$[HA]_b = \frac{[S]_w [H^+]_w}{K_d (K_a + [H^+]_w)} \tag{g}$$

If K_a be so small as to be negligible in the sum $(K_a + [H^+]_w)$, we have (h)

$$[HA]_b = \frac{[S]_w}{K_d} \tag{h}$$

If $[H^+]_w = K_a$ we have (i)

$$[HA]_b = \frac{[S]_w}{2 K_d} \tag{i}$$

If $[H^+]_w$ be so small as to be negligible in the sum $(K_a + [H^+]_w)$, we have (j)

$$[HA]_b = \frac{[S]_w [H^+]_w}{K_d K_a} \tag{j}$$

When $[H^+]_w$ is *very* small relative to $K_d K_a$, $[HA]_b$ is very small relative to $[S]_w$.

These approximate relations formulate one of the most common of laboratory practices; namely, the extraction of organic acids from water solutions by means of organic solvents. Acidification of the aqueous phase to form the undissociated molecules from the salts may bring about an enormous increase in the concentration of the substance in the non-aqueous phase. Change of $[H^+]$ from $[H^+] = K_a$ to practically complete suppression of ionization doubles the relative concentration.

In case the dissociation constants of two acids are of very different orders of magnitude, a fractional separation can be accomplished by adjusting the hydrion concentration to a value between those of the two dissociation constants.

The strict application of the principle briefly outlined is frequently complicated by association of molecules in one phase, by considerable departures from Henry's law, etc. See further detail by Hill, p. 343 Taylor's *Treatise on Physical Chemistry*, and Murray (1923).

Donnan equilibria. An elementary example only will be given to illustrate a principle implicit in Gibbs' treatment of equilibria but brought

into prominence by the important work of Donnan (1911) and Donnan and Harris (1911).

Imagine a membrane, M, on one side of which there is an aqueous solution of hydrochloric acid and on the other side of which there is not only hydrochloric acid but an acid HR neither the undissociated molecule nor the anion of which can penetrate the membrane.

$$
\begin{array}{c|c|c}
\text{``inside''} & & \text{``outside''} \\
[H^+] & & \\
& & [H^+]_o \\
[Cl^-] & & \\
& M & [Cl^+]_o \\
[HR] & & \\
[R^-] & &
\end{array}
$$

The presence of R^- upon one side only will *tend* to produce asymmetry of electric charge on opposite sides of the membrane, and there will be a tendency toward the compensation of this both by redistribution of the diffusible ions and readjustment of the ionization of the HR: R^- system. Also the presence of HR and R^- upon one side only tends to diminish the partial molal free energy of the solvent. This will tend to be compensated by a movement of water which may occur until, at equilibrium, the counter hydrostatic pressure has contributed its part to the balancing.

To simplify the elementary discussion, assume that the species HR and R^- have so little effect on "osmotic pressure" that their contribution to this effect may be neglected. Also assume that the solutions are sufficiently near "ideal" to permit the use of concentrations rather than activities.[1]

Imagine in each solution a hydrogen electrode under one atmosphere pressure of hydrogen. The E. M. F. of this gas-cell will be determined in part by the ratio of the hydrion concentrations on the two sides and in part by the potential difference E_M across the membrane.

$$
\text{E. M. F.} = \frac{RT}{F} \, ln \, \frac{[H^+]_i}{[H^+]_o} + E_M
$$

We may also imagine two chloride electrodes. For this cell

$$
\text{E. M. F.} = \frac{RT}{F} \, ln \, \frac{[Cl^-]_o}{[Cl^-]_i} + E_M
$$

---

[1] An entanglement might occur in the use of activities were the electrostatic constraint neglected in applying the definition that the activities of a substance in two phases are the same when the substance will not of itself pass from one phase to the other.

But if the system as a whole has attained equilibrium, no work can be obtained by transfer of either hydrions or chloride ions and E. M. F. $= 0$ in each case. Then, since E_M is the same,

$$\frac{[H^+]_i}{[H^+]_o} = \frac{[Cl^-]_o}{[Cl^-]_i} \tag{a}$$

In general the ratio of the concentration of an anion in the "outside" solution to the concentration of that anion in the "inside" solution is the same as the ratio of the concentrations of any other anion "outside" and "inside" and is inversely proportional to the ratio of "outside" and "inside" concentrations of any cation.

Although asymmetry in the distribution of ions was supposed to be the origin of the membrane potential-difference, a considerable potential difference may be caused by such a small inequality of material that we may still assume the ordinary rule of electroneutrality *in* each solution. Then on one side (inside)

$$[R^-]_i + [Cl^-]_i = [H^+]_i \tag{b}$$

Also outside

$$[Cl^-]_o = [H^+]_o \tag{c}$$

Substitute the equivalents of $[Cl^-]_i$ and $[Cl^-]_o$ from (b) and (c) in equation (a) and obtain

$$[H^+]_i^2 - [H^+]_i [R^-]_i = [H^+]_o^2 \tag{d}$$

If, then, the "outside" and "inside" solutions *before* the attainment of equilibrium were of the *same* hydrion concentration, hydrions would diffuse inward for the hydrion concentration of the inside solution will be greater than that of the outside solution *at equilibrium*. (A quantity must be subtracted from $[H^+]_i^2$ in (d) to equal $[H^+]^2$.)

If the non-diffusible substance were an ampholyte, forming R^+ on the acid side of the isoelectric point, the above relations regarding $[H^+]_i$ and $[H^+]_o$ would be reversed on the acid side of the isoelectric point.

To indicate the magnitude of migrations with no chloride inside initially, assume that the membrane is placed so that the two solutions are of equal volume. Between the initial and final states of the system chloride ions have diffused from right to left (see scheme below) till the concentration $[Cl^-]_3$ is x.

Initial state	$[HR]_1$ $[R^-]_1$ $[H^+]_1$	M		$[Cl^-]_2$ $[H^+]_2$
Equilibrium state	$[HR]_3$ $[R^-]_3$ $[H^+]_3$ $[Cl^-]_3$	M		$[Cl^-]_4$ $[H^+]_4$

Then

$$[H^+]_3 = [H^+]_1 + x \text{ and } [H^+]_4 = [H^+]_2 - x$$

or, since at equilibrium

$$\frac{[H^+]_3}{[H^+]_4} = \frac{[Cl^-]_4}{[Cl^-]_3},$$

$$\frac{[H^+]_1 + x}{[H^+]_2 - x} = \frac{[H^+]_2 - x}{x}$$

Whence

$$x = \frac{[H^+]_2^2}{[H^+]_1 + 2[H^+]_2}$$

The following table will give an idea of the magnitude of the effects due to the conditions assumed.

As we have already indicated, the difference of potential between two hydrogen electrodes placed on opposite sides of the membrane must, at the equilibrium state of the system, be equal and opposite to the potential difference at the membrane. Hence the membrane potential difference may be expressed *in terms of* a hydrogen electrode gas chain:

$$- \frac{RT}{F} \ln \frac{[H^+]_3}{[H^+]_4}.$$

By using this relation we calculate the membrane potential difference given in millivolts in the last column of the following table.

$[R^-]_1 = [H^+]_1$	$[H^+]_2$	INITIAL RATIO $\dfrac{[H^+]_1}{[H^+]_2}$	PER CENT HCl DIFFUSED TO ESTABLISH EQUILIBRIUM	EQUILIBRIUM DISTRIBUTION RATIO $\dfrac{[H^+]_3}{[H^+]_4}$	MEMBRANE POTENTIAL IN MILLIVOLTS
0.01	1.0	0.01	49.8	1.01	− 0.3
1.0	1.0	1.0	33.3	2.0	− 18.0
1.0	0.01	100.0	0.98	101.0	−120.0

Of course the conditions assumed for purposes of illustration are extremely simple but they suffice to indicate the nature of relations of very great importance in the physiology of the living cell.

The equations should be used with activities if strictly applied.

For one of many illustrations of the application, see Van Slyke (1926).

Ecology. Cells living in intimate contact with an aqueous solution are found to be dependent in various degree and various manner upon the hydrion concentration of the solution. See the manifold aspects illustrated by the texts of references under *Bacteriology*.

Likewise organisms drawing sustenance from the soil are found to be dependent upon the "soil reaction" as determined by measurements of aqueous extracts. See *Soils*. The more complex multicellular organisms may in some instances respond directly to the hydrion concentration of the environment but more often they are indirectly affected through the effects upon organized and unorganized foodstuffs. Through this complex chain, the distribution of the higher forms of life exhibits a considerable degree of correlation with the pH values of the natural waters or soils with which they are associated.

The literature on reaction as an ecological factor has now reached considerable bulk, and only a few typical articles can be noted here: *Fungi*, Waksman (1924); *Marine Algae*, Legendre (1925); *Fresh Water Algae*, Wehrle (1927); *Liverworts*, Dop and Chalaud (1926); *Ferns*, Wherry (1920–1921); *Coniferous trees*, Hesselman (1926); *Higher plants*, O. Arrhenius (1920), Atkins (1922), Wherry (1920), Olsen (1923), Chodat (1924), Christophersen (1925); *Earthworms*, O, Arrhenius (1921); *Snails*, Atkins and Lebour (1923); and *Fish*, Coker (1925). See especially the book by Mevius (1927).

Electrophoresis (cataphoresis) and electro-osmosis. An electrically charged body placed between an anode and a cathode will tend to move toward the pole having a charge opposite in sign to the charge on the body. If the body is a simple ion, the movement is called ionic migration. If the body is a particle suspended in a medium such as water, the movement is called electrophoresis. More generally it is known as cataphoresis. The distinction between ionic migration and electrophoresis is not always clear in the case of material in the colloidal state.

We shall not discuss the various theories advanced to account for the experimental facts but shall treat briefly only that point of view which it will be profitable to investigate further with the aid of methods for determining pH.

Since acidic or basic ionization may determine the sign of the charge upon a body of amphoteric nature the sign may be a function of the pH of the medium. The direction of electrophoresis is then a function of pH. At the isoelectric point electrophoresis is a minimum. The method of electrophoresis is useful in determining isoelectric points.

There can be no movement such as that noted above without a reciprocal interaction between suspended or dissolved material and the dispersing medium. If then the charged particles are fixed in position, as in the form of a porous diaphragm, are placed in water and the whole subjected to a potential gradient, the water will tend to move (electro-osmosis). The same *relative* relations indicated above then hold. If the diaphragm is of an amphoteric nature the direction of water flow will depend upon the acidic and basic properties of the diaphragm and upon pH of the aqueous phase.

In either one of the two cases (particles fixed or free to move) the same end result will be obtained if the particles adsorb hydrogen and hydroxyl ions according to their adsorption isotherms. Equality of adsorption

TABLE 71

Optimal reactions for the activity of various enzymes

(After Waksman and Davison, 1926)

ENZYME	SOURCE	OPTIMAL pH
Amylase (diastase)....	Asp. niger	3.5–5.5
	Duodenal contents (infants)	6.0–8.0 (viscosity)
	Malt	4.4–4.5
	Pancreas	7.0
	Potato juice	6.0–7.0
	Saliva	5.6 (acetate buffer)
		6.6 (phosphate buffer)
Arginase..............	Liver	10.0
Carboxylase...........	Yeast	5.3–6.2
Catalase..............	Blood	7.5 (10 minutes)
	Liver	7.0
	Vegetables	7.0–10.0
Emulsin..............	——	4.4
Erepsin..............	Intestine (pig)	7.9 (glycyl-glycin)
	Intestine (pig)	8.6 (conductivity method)
	Intestine (dog)	7.7 (albumose)
	Ox spleen	7.5–8.5
	Yeast	7.8
Invertase............	Asp. niger	2.5–3.5
	Potato juice	4.0–5.0
	Yeast	4.4–4.6 (52.1°C.)
	Yeast	4.2 (22.3°C.)
	Fresh yeast cells	4.2–5.2
Lipase..............	Blood	7.8–8.6
	Duodenal juice	5.0
	Duodenal juice	8.5
	Gastric juice	4.0–5.0
	Gastric juice of dog	4.9 (2.5 to 8.0)
	Serum	7.0–8.6
Maltase..............	Asp. oryzae	3.0 (35.5°C.)–7.2 (47°C.)
	Asp. oryzae	4.0
	Beer yeast	6.6
Oxidase..............	Vegetables	7.0–10.0
Pancreatin (trypsin-erepsin)............	Ox pancreas	9.7 (gelatin liquef. 37°C.)
	Ox pancreas	7.7–8.0 (peptone decomp.)
Pectase..............	Fruit	4.3

TABLE 71—*Concluded*

ENZYME	SOURCE	OPTIMAL pH
Pepsin...............	Animal tissues	3.0–3.5 (gelatin)
	Stomach	1.2–1.6 (acid albumin)
	Stomach	1.4 (edestin)
	Yeast	4.0–4.5
Peroxidase............	Vegetables	7.0–10.0
Protease.............	*Asp. oryzae*	5.1
	Autolyzing animal tissue	4.5
	Bacteria	6.0–7.0
	Malt	3.7–4.2
	Malignant human and rat tumors	7.0
	Papain	5.0–7.0
Rennet (lab)..........	Stomach	5.0
	Stomach	6.0–6.4
Trypsin..............	Animal tissues	7.8 (peptone)
	Pancreas	9.5
	Pancreas	8.3 (casein)
	Pancreas	7.5–8.3 (fibrin)
	Yeast	7.0 (peptone)
	Yeast	8.0
Urease................	Soy bean	About 7.0
Zymase..............	Living yeast	4.5–5.5 (28°C., no nitrogen)
	Living yeast	4.5–6.5 (28°C., plus yeast water)

and consequently equality of electrical charge is attained at a definite pH value. The position of such an "isoelectric" point is a function of the properties of the material and may lie anywhere along the pH scale (according to the nature of the material) with a narrow or broad isoelectric zone.

See, for examples, Gyemant (1921), Michaelis and Perlzweig (1926), Northrop and De Kruif (1921–1922), Winslow, and Falk, and Caulfield (1923), Porter (1921).

Enzymes. The influence of hydrogen ion concentration, or activity, upon the properties of enzymes has been the subject of an enormous number of investigations since the classic paper of Sørensen (1909). Data pertaining to specific enzymes may be traced through the comprehensive treatise, *Die Fermente* edited by Oppenheimer. This is now (1928) appearing in sections. A discussion of enzymes as electrolytes and as colloids is found in *Chemie der Enzyme* I, 3 aufl. by v. Euler (1925) see also Fodor

(1926), Rona (1926), and in Waksman and Davison's *Enzymes* (1926). See also K. G. Falk (1924). Table 71 is part of that compiled by Waksman and Davison, whose book should be consulted for references.

Foods. Considerable variation in pH values of food extracts, juices, etc., is of importance to canning (see Canning),[2] to thermal destruction of vitamines [See LaMer (1921), Sherman and Burton (1926) and Zilva (1923)] and to numerous industrial treatments of food-stuffs.

pH-values of various foods are given by Bigelow and Cathcart (1921), E. H. Harvey (1924).

The relative quantities of inorganic anions and cations and of acids or bases which can be "burned" to products which can be eliminated by the lungs or must be eliminated by the kidney are important to the study of acid-base metabolism and "neutrality"-regulation. See Blatherwick (1914).

Filtration. Hydrogen ion concentration, through its influence upon the dispersion of certain colloids and upon the conditioning of filter material, may control the filterability of a substance. Holderer's thesis from Perrin's laboratory presents in admirable form many of the theoretical aspects of the subject. The subject is not only of considerable theoretical interest but also of great practical importance. Buffer control with indicator tests may in many instances facilitate filtrations upon an industrial as well as a laboratory scale. See Electrophoresis.

Glass, effect of, on reaction of solutions. Many glasses contain so much "free-alkali" that they can seriously affect the pH value of poorly buffered solutions, especially when used as containers during heating. See, as examples, Esty and Cathcart (1921), Fabian (1921), Êwe (1920).

Hydrolysis of salts. Inspection of several titration curves discussed in previous chapters will show that, when equivalents of a univalent acid and a univalent base are mixed, the solution has a pH-value which is seldom that of "neutrality" and varies with the salt. Instead of estimating such values in the manner described in Chapter XXVIII, it is now desired to treat the subject from the following point of view. The preformed salt is used to construct the solution. Now the reaction between an acid and a base is reversible

$$HA + BOH \rightleftharpoons BA + H_2O$$

Consequently, if the preformed salt, BA, be used, it will react with water to some extent and will form some acid, HA, and base, BOH. The consequent splitting of water is the occasion for speaking of a *hydrolysis*.

The resulting acid, HA, and base, BOH, ionize. The ionization of the acid tends to increase the hydrogen ion concentration, and the ionization of the base tends to increase the hydroxyl ion concentration. If these tendencies are equal, the pH value of the original water will not be altered except through the effect of the salt upon K_w (see page 46). If the acid is "stronger" than the base, pH will be lessened and if the base is "stronger"

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[2] See page 576.

than the acid, pH will be increased. For detail return to the method of Chapter XXVIII.

Hydroxides of the metals, precipitation of. See *solubility product* and *precipitations*. Were the precipitates formed from solutions of metal salts by the addition of strong alkalies, true hydroxides of the type $M(OH)_n$, the treatment would be simple and could be illustrated in outline by graphs such as that of figure 100, page 582. There would then be a fairly narrow zone of pH within which a metal hydroxide having a characteristic solubility product would be precipitated. Undoubtedly the simple rela-
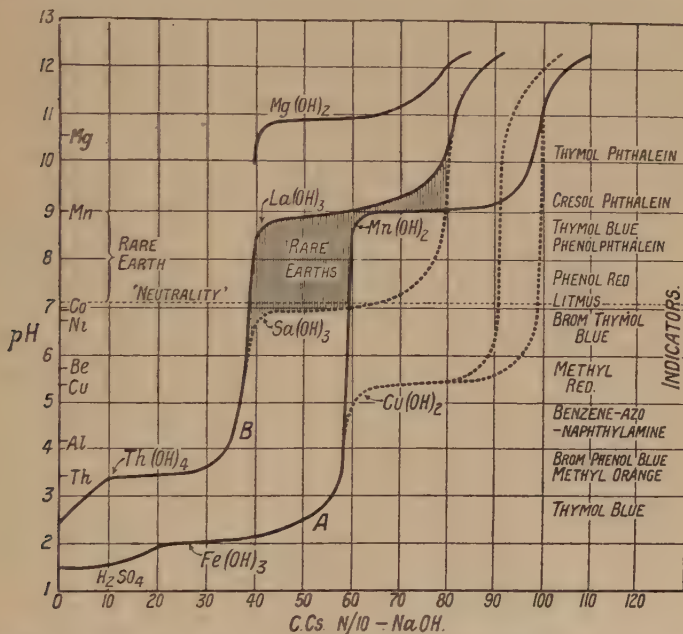
FIG. 98. BRITTON'S CURVES SHOWING ZONES OF PRECIPITATION OF METAL HYDROXIDES

tions then obtaining may be used to *outline one* of the chief aspects of the problem. However, many of the precipitates carry down the anion, are not true hydroxides and must be regarded either as solid solutions or treated by the methods of colloid chemistry. In a few instances only are there evidences of a definite chemical compound of constant composition *within* the zone of precipitation and before the true hydroxide is formed. Hence much of the literature regarding definite "basic salts" must be revised. Britton (1925) has assembled highly interesting preliminary data on the zones of pH within which the precipitates are formed. While it is impossible to tabulate extensive data here, there may be repro-

duced Britton's set of curves (fig. 98) showing the approximate location of zones of precipitation. Trace the more specialized literature through Britton's references and texts of analytical methods.

Immunity. Since substances concerned in immunological reactions are the protein antigens, are protein-like or are found in solutions containing proteins on which they are believed to be adsorbed or with which they are believed to be in combination, pH control and measurement find frequent application. But the literature is vast and the references therein to our subject are too frequent for review. A few references will be cited by way of illustration: Brooks (1920), Coulter (1920–1922), Defries and McKinnon (1926), DeKruif and Northrop (1922), A. Evans (1922), Falk and Caulfield (1923), Falk and Powdermaker (1925), Felton and Dougherty (1924), Hirsch (1922–1924), Homer (1917), Mason (1922), Michaelis and Davidsohn (1912), Mond (1927), Shaffer (1924), Sobotka and Friedlander (1928), Watson and Wallace (1924). See also Wells (1925).

Industrial uses. The most direct applications are in the manufacture of salts such as KH_2PO_4, titration of acids or bases for yields, extractions as of alkaloids (see distribution coefficients) and the control of reaction rates and equilibria. Processes in which complex equilibria are involved are exemplified by the treatment of boiler water, see Greer and Parker (1926) and the coagulation processes of water purification, see Buswell (1927). Pickling solutions are frequently put under automatic control.

The leather industry furnishes an example of the application of the physical chemistry of proteins, in the development of which pH-measurements have had a leading part. See book by Wilson (1928). In the bread industry pH-control has played an important part. Glutin is conditioned and the activity of yeast and the evolution of CO_2 from baking powders are conditioned by the hydrion concentration of the dough. Adequate pH control may hold in check the "rope" organism (Henderson, 1918) and Cohn et al. See review by Sørensen (1924). Cf., for examples, Green and Bailey (1927) and mill control by Weaver (1925).

As originally outlined in older terms by Pasteur, the "reaction" of wort and of must have much to do with the brewing of beer and wine fermentation. The control of "diseases" of beer and wine and the conditioning of the proteins held in solution are controllable by pH methods. See innumerable journal articles on brewing, for example, Emslander (1915–1919), Hulton (1924), R. H. Hopkins (1925), N. Parsons (1924), Windish, Dietrich and Kolbach (1922), and Ventre's (1925) book on wine.

The gelation optimum of pectin is pH 3.0 and the optimum of pectase is 4.3. For these reasons pH control is important in the manufacture of jellies. See for examples Tarr (1923) and Lüers and Lochmüller (1927).

Heat-penetration, temperature, holding-time and the hydrion concentration of the food have been so correlated with the death-rates of various bacteria that economy and certainty in commercial canning of foods can be assured. See Bigelow et al., Rogers, Deysher and Evans (1921).

The fermentation industries have continuous use for pH measurements. See "Bacteriology" and "Enzymes."

In the sizing of paper and other processes of the **paper** industry pH measurements are used. See Shaw (1925), Atsuki and Nakamura (1927).

Some processes incidental to the **textile** industry in which pH measurements are useful have been cited by Trotman (1926), Sacks (1927) and Strachan (1926), King (1927).

Wilson, Copeland and Heisig (1923) and Cobrum (1927) give examples of application in **sewage** treatment. See Buswell (1927).

Lyon, Fron and Fournier (1927) describe pH measurements as a means of judging **wood.**

A very active field of application is in the **sugar industry** where pH control of several steps has become an established practice. Among innumerable papers see Paine and Balch (1927), Perkins (1923), Aten, van-Ginneken and Engelhard (1926), Blowski and Holven (1925). The methods have been extended to uses of sugar such as **candy manufacture,** Sjostrom (1922).

The potential at which hydrogen is deposited freely upon an electrode is a function of the hydrogen ion concentration of the solution. Therefore, pH is important in controlling gassy deposits in **electroplating.** In addition it is found that buffer solutions, maintaining the pH within definite limits, aid in the production of desirable qualities of deposits, especially of nickel. See Thompson (1922), book by Blum and Hogaboom (1924), Montillon and Cassel (1924) and Britton's sketch (1927).

On **dry cells** see Holler and Ritchie (1920).

In **corrosion** the activity of hydrions plays an important part. See review by Bancroft (1924) and Corrosion Symposium (1925).

To a greater or lesser degree pH methods have been employed in the study of **cements** (Lerch and Bogue (1927); **exchange silicates,** see Jenny (1927) and Sweeney and Riley (1926); **commercial carbons,** see Hauge and Willaman (1927), Miller (1928); the catalytic decomposition of **explosives,** Farmer (1920), Angeli and Errani (1920); **rubber latex,** Freundlich and Hausen (1925), Bishop (1927); **clay,** Fessler and Kraner (1927), Randolph and Donnenwirth (1926) and Oakley (1927) and innumerable other subjects.

Additional references on several of the subjects mentioned above are to be found in W. A. Taylor's (1928) brochure. Parker (1927) has noted several instances where potentiometric control is used.

In innumerable cases the methods are applied to very incidental steps of important processes. In other cases acid-base equilibria are fundamental to a process. So varied are the examples of each type that the above sketch has little value other than to call attention to an enormous field.

Milk. A case exhibiting the *tendency* of physiological fluids to maintain constant ratio of dissociated to undissociated forms of acids and bases. Cow's milk is usually near pH = 6.5. Its variation is used as an index to diseased condition of udder, or, in market milk, to indicate spoilage. Complete description of acid-base equilibria of milk is lacking; cf. Clark (1927). For review of manifold applications of hydrion-methods in dairy science, see Rogers (1928).

Inorganic chemistry. Studies of inorganic equilibria involving hydrions are too numerous to mention.

Optical rotation. The specific rotation of an optically active acid, base or ampholyte may be distinct from that of its salt. Consequently the apparent specific rotation will vary as the solution passes through a zone of pH centered at the pK value. See figure 99. As examples of many studies which have been made, see Liquier (1925), Vlès *et al.* (1926), Levine *et al.* (1927).

Mutarotation, especially of sugar solutions, has long been known to be a function of the hydrion concentration of the solution. See treatment in modern terms by Brønsted and Guggenheim (1927), Lowry (1927), Kuhn and Jacob (1924).
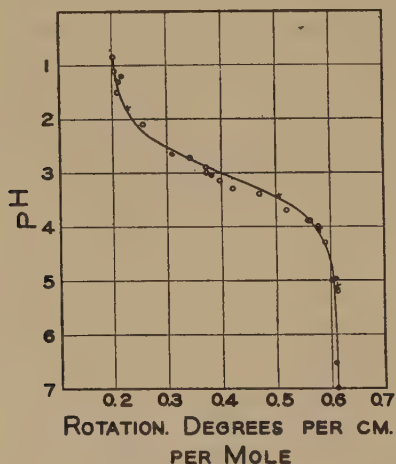
FIG. 99. ROTATION OF POLARIZED LIGHT BY TARTARIC ACID-TARTARATE SOLUTIONS AS A FUNCTION OF pH

(After Vlès and Vellinger (1925))

Organic chemistry. One of the common practices of organic chemistry is to modify the properties of a compound by substituting groups of acidic or basic nature and of different strength or by modifying the strength of such acidic or basic groups by the introduction of other groups which themselves are not acidic or basic. And yet one can search hundreds of articles or their abstracts before coming upon mention of the quantitative aspect which is susceptible to elaboration by the methods here described. Much of the material is assembled in texts on physical chemistry. The methods of measurement and control are frequently practiced unconsciously and as often practiced so much as a matter of course as to seem unworthy of special mention.

Permeability of membranes. In some instances the material of a membrane may be conditioned by the hydrion concentration of the solution with which it is in contact. Thereby its permeability in general may be altered. The question whether the ionized form or the undissociated residue of a particular substance is the form penetrating a given membrane is now receiving considerable attention. See, for example, Osterhout (1922). The participation of electrostatic forces in the distribution of ions between solution phase and membrane phase is discussed in a review by Michaelis (1926). Weber (1926) gives a bibliography 1922–1926. See also book by Stiles (1924).

Pharmacology, pharmaceutics, etc. Innumerable applications. Examples:

1. The active form of a drug may be the unionized form. See Michaelis and Dernby (1922), Dernby and Davide (1922), Trevan and Boock (1927).

2. The stability in solution may be a function of pH. See Levy and Cullen (1920), Stasiak (1926), Tainter (1926), Macht and Shohl (1920), Plant Research Lab. (1925).

3. The hydrolysis *in situ* may be a function of pH. See Shohl and Deming (1920).

4. The extraction from crudes may depend upon the partition coefficient of the ionized and non-ionized forms. See "Distribution Coefficients" and Fabre and Parinaud (1925),Evers (1922).

5. The preparation of a drug for injection may depend upon proper titration. See Elvove and Clark (1924).

6. The control of an organ used for test is dependent on the pH of the fluid. See "Physiology" and, for example, Gruber (1926).

See review by Jarisch (1926) and Brunius and Karsmark (1927).

Photographic processes. The most general material for suspending the silver halides is gelatine. In the manufacture of gelatine, pH control is advantageous. In the preparation of the emulsion, in determining the grain-growth of the suspended silver halide, in affecting that decomposition of thiourea derivatives which has to do with sensitizing, and in preventing hydrolysis of gelatine and reduction of silver salts, pH control is used. Swelling of gelatine is controlled by neutral salts as well as by pH.

Many of the dyes used as optical sensitizers are typical indicators and only the colored forms are effective. Control of pH on the one hand and adjustment of dissociation constants on the other hand have obvious uses.

The usual organic developers operate in alkaline solution. The reduction potentials of the systems are functions of $[H^+]$. Reaction velocity and "fog" are, in part, controlled by preventing excess alkalinity.

If the fixing bath of "hypo" (sodium thiosulfate) has a pH value less than about 4.0, the thiosulfate will decompose with liberation of sulfur. If the pH value is greater than 6.0, stains may result from fixation of iron compounds and reduction of silver by traces of developer. The fixing bath is, therefore, buffered in various ways.

"Temporary" hardening is controlled by salts and the acidity of the

solution. "Permanent" hardening by alums is similar to certain processes of tanning. The hardening effect of alum is a function of pH.

Indicators for photographic processes must in many cases show a useful color change in red or yellow light.

pH control is used in "after processes," e.g., intensification and reduction by increasing or diminishing the density of the deposit, in the bleaching of the reversal process, in toning and dyeing, and in transfer processes.

References: Rawlings (1926), Sheppard (1925–1926), Sheppard and Elliott (1923), Sheppard, Elliott and Sweet (1923), Wightman, Trivelli and Sheppard (1923).

Physiology, general. The classic examples of applications in this field are the description of the acid-base equilibria of the blood (see "Blood") and the control of enzyme activities (see "Enzymes"). But it is impracticable to enumerate all the other applications.

One of the most important applications of the principles discussed in this book is in the adjustment of **physiological salt solutions,** perfusion solutions, etc. Michaelis (1914) and others have called attention to the fact that some of the older solutions were not adequately buffered or adjusted. Improvement has been accomplished by the introduction of phosphate buffers or by making use of the equilibria of bicarbonate solutions under definite tensions of CO_2.

Among numerous papers on the subject may be mentioned those by A. C. Evans (1922), Fleisch (1922), Barkan, Broemser and Hahn (1922), Chopra and Sudhamoy (1925), Mason and Sanford (1924), and such discussions as are found in texts, e.g., Bayliss (1927).

In *Recent Advances in Physiology* (1926) Evans discusses the chemistry and physiology of **muscle** contraction and refers to the effect of pH on the recovery of muscle. See also McSwiney and Newton (1927) and Meyerhof (1923). Andrus and Carter (1927) conclude that cardiac tissue is peculiarly sensitive to alterations of hydrion concentration and that perhaps a difference of pH within and without the cell is a factor in excitation. Katz, Kerridge and Long (1925) find the buffering capacity of cardiac muscle is lower than that of skeletal muscle and that the critical level of pH is higher for the former. Evans (1926) reviews the evidence relating contraction to pH within and without the cell. On the zones of pH favorable to the several phases of heart action see Dale and Thacher (1914).

Gray (1922) finds that **ciliary** movement declines rapidly as the pH of the solution is lowered from about 7.2 to 6.0. Organic acids are more effective because of penetration. See Jacobs (1920). Pantin (1923) reviews **amoeboid** movement. See also Hopkins (1926) on locomotion of protozoa and Fenn (1922), Feringa (1923), and Jochims (1927) on **phagocytosis.** Clowes and Smith (1923) deal with the activity of **spermatozoa** in relation to the hydrion concentration of the medium. See also Gelhorn (1927), Kalwaryjski (1926), Anderson (1922), Healy (1922) and Vlès (1924).

Lillie and Shepard (1923) find that **heliotropism** of arenicola larvae is controlled by changes in the reaction of balanced isotonic solutions. See also Rose (1924).

Two important methods of attack on various problems of cell physiology are provided by the development on the one hand of Harrison's tissue culture and on the other hand of Barber's micro manipulation methods. Lewis and Felton (1922) and Fischer (1921) describe the uses of pH measurements in tissue culture while Chambers (1926–1927) describes the revelation of the pH of the cell interior which has come from the use of his improved methods of micro-injection. In a recent paper Chambers shows that the normal cytoplasmic pH of star fish eggs is 6.7 while that of the nucleus is 7.5. For comments on the relation of pH and reduction potentials of cell interior see Cohen, Chambers and Reznikoff (1928). The influence of pH on rates of reduction of methylene blue by tissues is discussed by Ahlgren (1925). The metabolism of the developing egg with reference to pH is discussed by Needham (1925). For notes on hen's eggs see Sharp and Whitaker (1927). For references on tumor cells see Warburg (1926).

Rous (1925–1927) (see Drury *et al.* 1927) has carried out an extensive study of the "relative reaction" of living mammalian tissues. But see Chambers. Mudd (1925) reports the effect of hydrion concentration upon electroendosmosis through mammalian serous membranes. For a review of plasmolysis see Prát (1926), and hemolysis, Mond (1927), Rockwood (1925).

The hydrion concentration of the medium is a controlling factor in the culture (Morea, 1927, Saunders, 1924), growth and locomotion (Hopkins, 1926) reproduction and encystment (Beers, 1927, Koffman, 1924) of protozoa. Pruthi (1927) shows the relation to protozoan sequence in hay infusions. Shapiro (1927), by feeding selected indicators to protozoa was able to assign definite values to the acidity of food vacuoles. See Stoll (1923) on hookworms and Jewell (1920) on tadpoles.

Bodine (1926) used a micro electrode in studying the blood of insects. See "Blood" for other references to the blood of lower animals.

On body fluids see brief mention in such texts as those of Höber (1927) and Kopacewski (1926), comments on general principles of exchange by Van Slyke (1926); McQuarrie and Shohl (1925) on cerebrospinal fluid; Talbert (1922) on sweat, etc.

Brief reviews of the rôle of hydrion concentration in several other phenomena must be sought in such general texts as that of Rogers (1927), Höber (1927), Bayliss (1927), but more particularly in the special literature.

In the field of Plant Physiology the applications have been numerous. Although it is difficult to separate subjects in this field from those referred to in the sections "Soils" and "Ecology," there may be mentioned, merely by way of illustration, the following subjects and references: **Absorption by plants**: Robbins (1926); **pH numbers of plant cells**; Pfeiffer (1927), Haas (1917), Atkins (1922–1924), Small (1926), Rea and Small (1927); **pH gradient**: Gustafsen (1924); **Photoperiodism**: Garner, Bacon and Allard (1924); **Turgor**: Pfeiffer (1927); **Staining**: Naylor (1926); **Chlorosis**: McCall and Haag (1921). An excellent review of several aspects of plant physiology in which pH measurements have been used is given

by Pfeiffer (1927).   Numerous investigations have been made of the rôle of reaction in the defense against parasites.   Examples are: Gillespie and Hurst (1918), Scott (1922–1924), McInnes, J. (1922), Berridge (1924) and Hurd (1924), Atkins (1922).

Precipitations. Usually an acidic ionogen is less soluble than its alkali salt and a basic ionogen is less soluble than its chloride.   Figure 100 illustrates in elementary outline phenomena that may occur in titrating the hydrochloride of a base.   The abscissa represents percentage neutralization of the hydrochloric acid combined with the base.   The equilibrium is given approximately by:

$$pH = 4.0 + \log \frac{[B]}{[BH^+]} \tag{a}$$
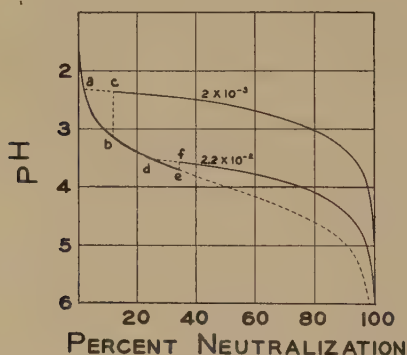
FIG. 100. TITRATION OF 100 CC. OF N/100 HYDROCHLORIDE OF A BASE

$(14\text{-}K_b = 4)$ WITH NaOH

Solubility of free base 2×10^{-3} in one case and 2.2×10^{-2} in the other case

Accordingly the type curve is plotted with center at pH = 4.0.

Suppose the solubility of the free base, [B], is 2×10^{-3}.   Then when the solid form has precipitated

$$pH = 4.0 - 2.7 - \log [BH^+] = 1.3 - \log [BH^+] \tag{b}$$

If 0.1 M hydrochloride of the base has been titrated to incipient precipitation, $[BH^+] = 0.1 - 0.002 = 0.098$ (neglecting dilution).   Hence pH = 2.3 which is point a of figure 100.   It may be that precipitation will not occur at once and that the solution will remain supersaturated to point b.   Then, with the formation of a precipitate, the pH value jumps back to c.   From then on the curve is determined by equation (b) approximately.

If the solubility of the free base is 2.2×10^{-2} precipitation will determine the following equation

$$pH = 4.0 - 1.66 - \log [BH^+] = 2.34 - \log [BH^+] . \tag{c}$$

Then at incipient precipitation $[BH^+] = 0.1 - 0.02 = 0.078$. Hence pH $= 3.54$ approximately. The titration curve may continue to c instead of "breaking" at d; but, with precipitation, the pH value will drop back to f.

The above description is approximate, not only because of the neglect of dilution and the use of the first approximation equation, but particularly because the activities were not used and no consideration was given to the effect of ionic strength of the solution upon solubility. Nevertheless the example illustrates how the "titration curve" is displaced to a greater or lesser extent depending upon the magnitude of the solubility of the precipitable component. It illustrates the flattening of the curve or increased buffer index in a narrowed zone. It also illustrates a method of determining solubility.

Recently Naegeli (1926) has given an extensive review of instances, chiefly from the field of colloid chemistry. He proposed to elevate to the rank of a new principle of acidimetry the employment of substances which precipitate at low concentrations and at definite zones of pH. He suggests in particular isonitrosoacetyl-p-amino azo benzene (indicator a) and isonitrosoacetyl-p-toluoazo-p-toluidine (indicator b). For these Naegeli finds the following ranges:

BUFFER SOLUTION	RANGE					
	Indicator a			Indicator b		
Borax-NaOH.....	turbid	10.95–11.01	clear	turbid	11.30–11.36	clear
Phosphate-NaOH.........	turbid	10.80–10.90	clear	turbid	11.55–11.63	clear
Glycocol-NaOH.........	turbid	10.91–10.98	clear	turbid	11.68–11.74	clear

Note the extremely narrow range. Since the zone lies near those values of pH which are required for the titration of certain weak acids by strong bases (see page 535) Naegeli had some success in this application.

Proteins. From what is known of their chemical structure, proteins are believed to be amphoteric. As such their conduct should be subject to the state of the acid-base equilibria of the solution in which they are dispersed. Because of the high molecular weights of proteins and the apparently numerous groups which can function as acids or bases, it is impracticable to formulate equations comparable to those of simple systems and to subject these to experimental test. For the same reason experimental progress in developing analogies with the equilibria of simple systems has required the most painstaking work. Such work is well exemplified in the classic papers of Sørensen and his coworkers which are to be found chiefly in Compt. rend. trav. lab. Carlsberg, 1917 to date. Beginning with the work of Hardy (1899–1905), Loeb (1909), Michaelis (1909), Chick (1913), Pauli (1903–date) and continuing through the later

work of these same authors, and of Cohn, Sørensen and numerous others, a large body of excellent working hypotheses and fundamental data has been accumulated. See such reviews as that of Cohn (1925) and Lloyd's book. Loeb reentered the field about 1918. His book (1922) contains interesting material more precisely formulated elsewhere.

As an example of the application of the Debye-Hückel equation to protein solutions see Cohn and Prentiss (1927) and Sørensen and Linderstrøm-Lang (1927).

Solubility, solubility product. The true solubility of a compound may be regarded as independent of the hydrogen ion concentration of the solution; but if the compound is an acid, a base or an ampholyte, some of the material present in solution may be ionized and the apparent solubility will include both the ionized and unionized forms. Therefore, the total or apparent solubility is a function of pH.

Since the presence of extraneous material often has a great influence upon the true solubility of a substance there is some advantage in starting the elementary formulation with the use of the activity-concept.

When the activities of a substance in two phases are the same the substance will not of itself pass from one phase to the other. Let the acid HA be present in a solid phase where the activity is $(HA)_s$.

$$(HA)_s = a \text{ constant} \tag{a}$$

The activity in the liquid phase will be the same at equilibrium.

$$(HA)_l = (HA)_s \tag{b}$$

In the liquid phase

$$\frac{(H^+)_l \, (A^-)_l}{(HA)_l} = K_a \tag{c}$$

or by (a), (b) and (c):

$$(H^+)_l \, (A)_l = a \text{ constant} = K_s \tag{d}$$

The constant K_s is called the solubility product.

Introducing activity coefficients, we have:

$$[H^+] \, [A^-] = \frac{K_s}{\gamma_{H^+} \, \gamma_{A^-}} \tag{e}$$

or

$$(H^+) = \frac{K_s}{\gamma_{A^-} \, [A^-]} \tag{e-2}$$

Chapter XXV deals with the calculation of activity coefficients and indicates that a first order approximation of their evaluation for very dilute solutions has been accomplished. See figure 86, page 504. This accounts for the influence of neutral salts of various valence-types at high

dilution; but in the presence of high concentrations of salts and other material the distribution of water is seriously affected and a "salting out" process may be superimposed. Inexplicable effects such as are observed when an organic solvent is but slightly altered by addition or withdrawal of a minute quantity of some solute are often encountered.

Soils. A water extract of a soil will have taken up acids, bases and salts in ratios conveniently described in terms of pH. A narrow range of pH values may be determined by the mineral constituents of the soil [see, for example, Kappen (1916)] by the products of leaf and wood decomposition [see, for example, Odén (1916)], by material excreted by plant roots [see, for example, Duggar (1920), Davidson and Wherry (1924)], by bacterial metabolism [see, for example, Waksman (1927)] or by artificial additions. In the absence of artificial additions there may be reached a natural balance in the contribution of each factor. This may permit a correlation between pH and soil-type [see, for example, Gillespie and Hurst (1918)] or between pH and plant-type [see references under *Ecology*].

The causal relation between the frequency of occurrence of a given plant species in soils of a narrow range of pH and the pH may be direct in some instances. More often it is probably indirect and is concerned with the influence of soil-reaction upon the micro-organisms concerned in supplying plant nutrition [see Waksman (1927)] or upon parasites [see, for example, Gillespie (1918)]. However, the end result is a zone of pH favorable for each given species of plant.

The importance of controlling the soil pH in agriculture is now widely recognized. Lime is frequently used to increase pH [see, for example, discussion by Hoagland and Christie (1918)] and sulfur (which oxidizes to H_2SO_4) to decrease pH [see discussion by Lipman, Waksman and Joffe, 1921].

Some data have been obtained in recent years on the optimum pH values for the production of individual crops. The most extensive of these studies is that of O. Arrhenius (1926). The pH values of 70,000 samples from 15,000 fields in which sugar beets were growing were determined. Both the highest yields and the maximum sugar contents were found uniformly in the range pH 7.0 to 7.5. A list of several hundred plants of agricultural and horticultural interest, arranged according to their optimum pH values, has been published by Wherry (1926).

There is now an enormous literature on the manifold aspects of the subject. The following reviews may be consulted. Fisher (1921), Knickmann (1925), Olsen (1923), Wherry (1922), Wiegner and Gessner (1926), Trénel (1927).

Staining and dyeing. Most dyestuffs are of basic or acidic nature. Many have ionization constants the values of which fall within the range of ordinary hydrogen ion concentrations. Systematic evaluations remain to be conducted. Many of the substances which "take" dyes are themselves basic or acidic. Consequently there are good grounds for believing that dyeing is in *some* measure salt formation. However, the ordinary equilibrium laws are inapplicable for account must be taken of the fact that

many dyes in the aqueous phase are dispersed in colloidial degree, of the fact that the material dyed is often surface-active and of the fact that dye-substrate "compounds" exhibit specific properties. There is here another instance where progress requires the close cooperation of various theoretical and experimental methods of approach.

Empirically, the control of hydrion concentrations and the study of the acidic or basic nature of the substrate have yielded information of considerable value, which should not be regarded as determinative of theory nor neglected by the theorist.

Examples: Agulhon and Léobardy (1921), Boissevain (1927), Collier (1924), Elöd (1925–1926), Gellhorn (1927), Haden (1923), Marker and Gordon (1924), Mommsen (1926), Naylor (1926), Pfeiffer (1927), Rohde (1920), Ruhland (1923), Sheppe and Constable (1923), Speakman (1924), Smith (1922), Stearn and Stearn (1924), Weiser and Porter (1927), Zirkle (1927), Bálint (1926).

Surface tension. See investigation and references by Hartridge and Peters (1922), Egnér and Hägg (1927) and general treatment by Rideal (1926).

Taste. One of the original means of distinguishing acids. See page 1. There has been considerable discussion of the function of $[H^+]$. See review by Dietzel (1926).

Water, distilled and "conductivity." Review by Bencowitz and Hotchkiss (1925); *cf.* Bordas and Touplain (1926), Kolthoff (1926), and Bjerrum (1927).

Waters, inland. The pH value of an inland water may be influenced by the deposits with which it comes in contact. For an extreme see Wells (1921). For the effect of stratification in lakes see Juday, Fred and Wilson (1924). For the effect of industrial wastes and sewage see Buswell (1927). See also "Ecology," Shelford (1925), Cowles and Schwitalla (1923), Saunders (1921).

Water, sea. The carbonate equilibrium *tends* to maintain sea water at a constant pH. This has doubtless varied with the CO_2-tension of the atmosphere in geological time. Locally it varies with temperature, the photosynthetic action of the flora, accretions from rivers, and contact with geologic deposits. The wider aspects have been described in Henderson's *Fitness of the Environment.* The charting of the pH values of different regions of the seas has been of aid in oceanographic surveys and of value to the study of plant and animal distribution. See treatises by Palitzsch (1922), Gaarder (1916–1917), Legendre (1926), Mayer (1922), Bresslau (1926), Atkins *et al.* (1924).

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know where we can find information upon it.*—Samuel Johnson.

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APPENDIX

Arbitrarily Standardized Values for Half-Cells
See Chapter XXIII and especially page 488.

Half-Cell I $\|$ (H$^+$) = 1 | H$_2$(1 atmos.), Pt.
Half-Cell II   KCl (sat.) | KCl (0.1 N), HgCl | Hg
Half-Cell III   KCl (sat.), HgCl | Hg
Half-Cell IV   KCl (sat.) | HCl (0.1 N) | H$_2$(1 atmos.), Pt.
Half-Cell V   KCl (sat.) | KHPhthalate (0.05 M) | H$_2$(1 atmos.), Pt.
Half-Cell VI   KCl (sat.) | Acetic acid (0.1 N) / Na Acetate (0.1 M) | H$_2$(1 atmos.), Pt.
Half-Cell VII $\|$ (H$^+$) = 1, quinhydrone | Pt.
Half-Cell VIII KCl (sat.) | HCl (0.1 N), quinhydrone | Pt.

TEMPER-ATURE	HALF-CELL							
	I	II	III	IV[a]	V	VI	VII	VIII
°C.	volts	volts	volts	volts	volts	volts	volts	volts
18	0.0000	0.3380	0.251	−0.0621	(−0.229)	−0.2668	0.7044	0.6423
20	0.0000	0.3379	0.250	−0.0625	−0.2310	−0.2686	0.7029	0.6404
25	0.0000	0.3376	0.2458	−0.0636	(−0.235)	−0.2732	0.6992	0.6356
30	0.0000	0.3371	0.242	−0.0647	(−0.239)		0.6955	0.6308
35	0.0000	0.3365	0.238	−0.0657			0.6918	0.6261
38	0.0000	0.3361	0.236	−0.0664			0.6896	0.6232
40	0.0000	0.3358	0.234	−0.0668			0.6881	0.6213

Examples of experimental values (see page 479)

CELL	TEMPER-ATURE	E	CITATION	CELL	TEMPER-ATURE	E	CITATION
	°C.				°C.		
II:III	18	0.087	Table	III:IV	25	0.3094	Table
		0.0885	Walpole, 1914			0.3103	Fales and Mudge, 1920
		0.0874	Michaelis, 1914			0.3102[g]	Harned, 1926
	25	0.0918	Table		38	0.3024	Table
		0.0918	Fales and Mudge, 1920			0.3024	Stadie and Hawes, 1928, maximum
		0.0916[b]	Ewing, 1925			0.3010	Stadie and Hawes, 1928, minimum
II:IV	18	0.4001	Table		40	0.3008	Table
		0.4011[c]	Sørensen and Linderstrøm-Lang, 1924			0.3016	Fales and Mudge, 1920
	25	0.4012[d]	Table	III:V	30	0.481	Table
		0.4010	Myers and Acree, 1913			0.482	Author
		0.4000	Loomis and Acree, 1911	III:VI	18	0.5178	Table
		0.4004	Harned, 1915			0.5175	Michaelis, 1914
		0.3995	Fales and Vosburgh, 1918		25	0.5190	Table
		0.4020	Fales and Mudge, 1920			0.5195	Michaelis, 1914
		0.3985[e]	Cohn and Berggren, 1925				
II:VI	18	0.6048	Table	VI:IV	18	0.2047	Table
		0.6046[f]	Walpole, 1914			0.2095[h]	Michaelis and Kakinuma, 1923
						0.2085[h]	Michaelis and Fujita, 1923

[a] Calculated with assumption that γ_{H^+} = 0.84 and neglect of junction potential.   [b] Calculated from data for Hg | HgCl, KCl (sat.) | KCl (1. N), HgCl | Hg.   [c] With 3.5 N KCl as bridge.   [d] 0.4009[g] calculated from Scatchard's data.   [e] Calculated.   [f] Uncorrected for barometer? Add 0.3 m.v.?   [g] Uncorrected for change from molal to molar.   [h] Special liquid junction.

TABLE B
SHOWING RELATION OF [H⁺] TO pH (ON THE ASSUMPTION THAT

$$pH = \text{Log} \frac{1}{[H^+]}\Big)$$

See Chapter XXIII

pH	[H⁺]	pH	[H⁺]	pH	[H⁺]
x.00	1.000×10^{-x}	x.35	0.447×10^{-x}	x.70	0.200×10^{-x}
x.01	0.977×10^{-x}	x.36	0.437×10^{-x}	x.71	0.195×10^{-x}
x.02	0.955×10^{-x}	x.37	0.427×10^{-x}	x.72	0.191×10^{-x}
x.03	0.933×10^{-x}	x.38	0.417×10^{-x}	x.73	0.186×10^{-x}
x.04	0.912×10^{-x}	x.39	0.407×10^{-x}	x.74	0.182×10^{-x}
x.05	0.891×10^{-x}	x.40	0.398×10^{-x}	x.75	0.178×10^{-x}
x.06	0.871×10^{-x}	x.41	0.389×10^{-x}	x.76	0.174×10^{-x}
x.07	0.851×10^{-x}	x.42	0.380×10^{-x}	x.77	0.170×10^{-x}
x.08	0.832×10^{-x}	x.43	0.372×10^{-x}	x.78	0.166×10^{-x}
x.09	0.813×10^{-x}	x.44	0.363×10^{-x}	x.79	0.162×10^{-x}
x.10	0.794×10^{-x}	x.45	0.355×10^{-x}	x.80	0.158×10^{-x}
x.11	0.776×10^{-x}	x.46	0.347×10^{-x}	x.81	0.155×10^{-x}
x.12	0.759×10^{-x}	x.47	0.339×10^{-x}	x.82	0.151×10^{-x}
x.13	0.741×10^{-x}	x.48	0.331×10^{-x}	x.83	0.148×10^{-x}
x.14	0.725×10^{-x}	x.49	0.324×10^{-x}	x.84	0.144×10^{-x}
x.15	0.708×10^{-x}	x.50	0.316×10^{-x}	x.85	0.141×10^{-x}
x.16	0.692×10^{-x}	x.51	0.309×10^{-x}	x.86	0.138×10^{-x}
x.17	0.676×10^{-x}	x.52	0.302×10^{-x}	x.87	0.135×10^{-x}
x.18	0.661×10^{-x}	x.53	0.295×10^{-x}	x.88	0.132×10^{-x}
x.19	0.646×10^{-x}	x.54	0.288×10^{-x}	x.89	0.129×10^{-x}
x.20	0.631×10^{-x}	x.55	0.282×10^{-x}	x.90	0.126×10^{-x}
x.21	0.617×10^{-x}	x.56	0.275×10^{-x}	x.91	0.123×10^{-x}
x.22	0.603×10^{-x}	x.57	0.269×10^{-x}	x.92	0.120×10^{-x}
x.23	0.589×10^{-x}	x.58	0.263×10^{-x}	x.93	0.117×10^{-x}
x.24	0.575×10^{-x}	x.59	0.257×10^{-x}	x.94	0.115×10^{-x}
x.25	0.562×10^{-x}	x.60	0.251×10^{-x}	x.95	0.112×10^{-x}
x.26	0.549×10^{-x}	x.61	0.245×10^{-x}	x.96	0.110×10^{-x}
x.27	0.537×10^{-x}	x.62	0.240×10^{-x}	x.97	0.107×10^{-x}
x.28	0.525×10^{-x}	x.63	0.234×10^{-x}	x.98	0.105×10^{-x}
x.29	0.513×10^{-x}	x.64	0.229×10^{-x}	x.99	0.102×10^{-x}
x.30	0.501×10^{-x}	x.65	0.224×10^{-x}	1 + x.00	0.100×10^{-x}
x.31	0.490×10^{-x}	x.66	0.219×10^{-x}	1 + x.01	0.0977×10^{-x}
x.32	0.479×10^{-x}	x.67	0.214×10^{-x}	1 + x.02	0.0955×10^{-x}
x.33	0.468×10^{-x}	x.68	0.209×10^{-x}		
x.34	0.457×10^{-x}	x.69	0.204×10^{-x}		

Examples: $pH = 7.00$; $[H^+] = 1.000 \times 10^{-7}$
$\qquad pH = 6.63$; $[H^+] = 0.234 \times 10^{-6} = 2.34 \times 10^{-7}$
$\qquad [H^+] = 1.23 \times 10^{-8}$; $pH = 7.91$

See Klopsteg (1921).

TABLE C

FACTORS FOR CONCENTRATION CELLS 0°C TO 70°C.

$$E = 0.000{,}198{,}322 \; T \log \frac{C_1}{C_{\mathrm{II}}} \quad \text{(when valence = 1).} \quad A = 0.000{,}198{,}322 \; T.$$

See discussion page 250 for uncertainties.

t (CENTIGRADE)	T (ABSOLUTE)	A	$\dfrac{1}{A}$ *	LOG A
0	273.1	0.054162	18.463	$\bar{2}$.7336935
1	274.1	0.054360	18.396	$\bar{2}$.7352808
2	275.1	0.054558	18.329	$\bar{2}$.7368624
3	276.1	0.054757	18.263	$\bar{2}$.7384382
4	277.1	0.054955	18.197	$\bar{2}$.7400083
5	278.1	0.055153	18.131	$\bar{2}$.7415728
6	279.1	0.055352	18.066	$\bar{2}$.7431316
7	280.1	0.055550	18.002	$\bar{2}$.7446849
8	281.1	0.055748	17.938	$\bar{2}$.7462326
9	282.1	0.055947	17.874	$\bar{2}$.7477749
10	283.1	0.056145	17.811	$\bar{2}$.7493117
11	284.1	0.056343	17.748	$\bar{2}$.7508430
12	285.1	0.056542	17.686	$\bar{2}$.7523690
13	286.1	0.056740	17.624	$\bar{2}$.7538897
14	287.1	0.056938	17.563	$\bar{2}$.7554050
15	288.1	0.057137	17.502	$\bar{2}$.7569151
16	289.1	0.057335	17.441	$\bar{2}$.7584199
17	290.1	0.057533	17.381	$\bar{2}$.7599195
18	291.1	0.057732	17.321	$\bar{2}$.7614140
19	292.1	0.057930	17.262	$\bar{2}$.7629034
20	293.1	0.058128	17.203	$\bar{2}$.7643876
21	294.1	0.058327	17.145	$\bar{2}$.7658668
22	295.1	0.058525	17.087	$\bar{2}$.7673410
23	296.1	0.058723	17.029	$\bar{2}$.7688102
24	297.1	0.058921	16.972	$\bar{2}$.7702745
25	298.1	0.059120	16.915	$\bar{2}$.7717338
26	299.1	0.059318	16.858	$\bar{2}$.7731882
27	300.1	0.059516	16.802	$\bar{2}$.7746378
28	301.1	0.059715	16.746	$\bar{2}$.7760826
29	302.1	0.059913	16.691	$\bar{2}$.7775225
30	303.1	0.060111	16.636	$\bar{2}$.7789577
31	304.1	0.060310	16.581	$\bar{2}$.7803882
32	305.1	0.060508	16.527	$\bar{2}$.7818140
33	306.1	0.060706	16.473	$\bar{2}$.7832351
34	307.1	0.060905	16.419	$\bar{2}$.7846516
35	308.1	0.061103	16.366	$\bar{2}$.7860635
36	309.1	0.061301	16.313	$\bar{2}$.7874708
37	310.1	0.061500	16.260	$\bar{2}$.7888736
38	311.1	0.061698	16.208	$\bar{2}$.7902718
39	312.1	0.061896	16.156	$\bar{2}$.7916656
40	313.1	0.062095	16.104	$\bar{2}$.7930549
45	318.1	0.063086	15.851	$\bar{2}$.7999355
50	323.1	0.064078	15.606	$\bar{2}$.8067088
55	328.1	0.065069	15.368	$\bar{2}$.8133780
60	333.1	0.066061	15.137	$\bar{2}$.8199464
65	338.1	0.067053	14.914	$\bar{2}$.8264170
70	343.1	0.068044	14.696	$\bar{2}$.8327925

* Useful in machine calculations.

TABLE D
Correction of Barometer Reading for Temperature

When the mercury in the barometer is at the temperature t subtract the following millimeters to obtain the barometic height in terms of mercury at zero degrees centigrade.

t	BAROMETER READINGS IN MILLIMETERS						
	720	730	740	750	760	770	780
17	2.0	2.0	2.1	2.1	2.1	2.1	2.2
18	2.1	2.1	2.2	2.2	2.2	2.3	2.3
19	2.2	2.3	2.3	2.3	2.4	2.4	2.4
20	2.3	2.4	2.4	2.4	2.5	2.5	2.5
21	2.5	2.5	2.5	2.6	2.6	2.6	2.7
22	2.6	2.6	2.7	2.7	2.7	2.8	2.8
23	2.7	2.7	2.8	2.8	2.8	2.9	2.9
24	2.8	2.9	2.9	2.9	3.0	3.0	3.1
25	2.9	3.0	3.0	3.1	3.1	3.1	3.2
26	3.0	3.1	3.1	3.2	3.2	3.3	3.3
27	3.2	3.2	3.3	3.3	3.3	3.4	3.4
28	3.3	3.3	3.4	3.4	3.5	3.5	3.6
29	3.4	3.4	3.5	3.5	3.6	3.6	3.7
30	3.5	3.6	3.6	3.7	3.7	3.8	3.8
31	3.6	3.7	3.7	3.8	3.8	3.9	3.9

For various refined corrections of barometric readings see article on Barometry and Manometry by Kimball in *International Critical Tables*, Vol. 1, p. 68.

TABLE E

BAROMETRIC CORRECTIONS FOR H-ELECTRODE POTENTIALS

(Data for use in plotting correction curves) .

$$E_{bar.} = \frac{0.000,198322\ T}{2} \log \frac{760}{x}$$

TEMPER-ATURE	CORRECTED PRESSURE	VAPOR PRESSURE	x	$\log \frac{760}{x}$	$E_{bar.}$
°C.	mm.	mm.			millivolts
12	780	10.5	769.5	−0.00537	−0.15
	760		749.5	+0.00604	+0.17
	740		729.5	0.01779	0.50
18	780	15.5	764.5	−0.00256	−0.07
	760		744.5	+0.00895	+0.26
	740		724.5	0.02078	0.60
20	780	17.5	762.5	−0.00143	−0.04
	760		742.5	+0.01012	+0.29
	740		722.5	0.02198	0.64
25	780	23.8	756.2	0.00218	0.06
	760		736.2	0.01382	0.41
	740		716.2	0.02578	0.76
30	780	31.8	748.2	0.00680	0.20
	760		728.2	0.01856	0.56
	740		708.2	0.03066	0.92
35	780	42.2	737.8	0.01288	0.39
	760		717.8	0.02481	0.76
	740		697.8	0.03708	1.13
40	780	55.3	724.8	0.02060	0.64
	760		704.8	0.03275	1.02
	740		684.7	0.04525	1.41

$$\frac{E.\ M.\ F. + E_{bar.} - E_{cal.}}{0.000,198322\ T} = pH$$

TABLE F

VALUES OF LOG $\dfrac{\alpha}{1-\alpha}$ AND OF LOG $\dfrac{\alpha}{1-\alpha}$ MULTIPLIED BY THE TEMPERATURE FACTORS FOR CONCENTRATION CELLS AT 20°, 25°, 30° AND 37.5°C.

α	LOG $\dfrac{\alpha}{1-\alpha}$	LOG $\dfrac{\alpha}{1-\alpha}$ MULTIPLIED BY			
		0.058128 (20)	0.059120 (25)	0.060111 (30)	0.061599 (37.5)
0.001	-2.9996	-0.1744	-0.1773	-0.1803	-0.1848
0.005	-2.2989	-0.1336	-0.1359	-0.1382	-0.1416
0.01	-1.9956	-0.1160	-0.1180	-0.1200	-0.1229
0.02	-1.6902	-0.0982	-0.0999	-0.1016	-0.1041
0.03	-1.5096	-0.0878	-0.0892	-0.0907	-0.0930
0.04	-1.3802	-0.0802	-0.0816	-0.0830	-0.0850
0.05	-1.2788	-0.0743	-0.0756	-0.0769	-0.0788
0.06	-1.1950	-0.0695	-0.0706	-0.0718	-0.0736
0.07	-1.1234	-0.0653	-0.0664	-0.0675	-0.0692
0.08	-1.0607	-0.0617	-0.0627	-0.0638	-0.0653
0.09	-1.0048	-0.0584	-0.0594	-0.0604	-0.0619
0.10	-0.9542	-0.0555	-0.0564	-0.0574	-0.0588
0.11	-0.9080	-0.0528	-0.0537	-0.0546	-0.0559
0.12	-0.8653	-0.0503	-0.0512	-0.0520	-0.0533
0.13	-0.8256	-0.0480	-0.0488	-0.0496	-0.0509
0.14	-0.7884	-0.0458	-0.0466	-0.0474	-0.0486
0.15	-0.7533	-0.0438	-0.0445	-0.0453	-0.0464
0.16	-0.7202	-0.0419	-0.0426	-0.0433	-0.0444
0.17	-0.6886	-0.0400	-0.0407	-0.0414	-0.0424
0.18	-0.6585	-0.0383	-0.0389	-0.0396	-0.0406
0.19	-0.6297	-0.0366	-0.0372	-0.0379	-0.0388
0.20	-0.6021	-0.0350	-0.0356	-0.0362	-0.0371
0.21	-0.5754	-0.0334	-0.0340	-0.0346	-0.0354
0.22	-0.5497	-0.0320	-0.0325	-0.0330	-0.0339
0.23	-0.5248	-0.0305	-0.0310	-0.0315	-0.0323
0.24	-0.5006	-0.0291	-0.0296	-0.0301	-0.0308
0.25	-0.4771	-0.0277	-0.0282	-0.0287	-0.0294
0.26	-0.4543	-0.0264	-0.0269	-0.0273	-0.0280
0.27	-0.4320	-0.0251	-0.0255	-0.0260	-0.0266
0.28	-0.4102	-0.0238	-0.0243	-0.0247	-0.0253
0.29	-0.3888	-0.0226	-0.0230	-0.0234	-0.0239
0.30	-0.3680	-0.0214	-0.0218	-0.0221	-0.0227
0.31	-0.3475	-0.0202	-0.0205	-0.0209	-0.0214
0.32	-0.3274	-0.0190	-0.0194	-0.0197	-0.0202
0.33	-0.3076	-0.0179	-0.0182	-0.0185	-0.0189
0.34	-0.2880	-0.0167	-0.0170	-0.0173	-0.0177
0.35	-0.2688	-0.0156	-0.0159	-0.0162	-0.0166
0.36	-0.2499	-0.0145	-0.0148	-0.0150	-0.0154
0.37	-0.2311	-0.0134	-0.0137	-0.0139	-0.0142
0.38	-0.2126	-0.0124	-0.0126	-0.0128	-0.0131
0.39	-0.1943	-0.0113	-0.0115	-0.0117	-0.0120
0.40	-0.1761	-0.0102	-0.0104	-0.0106	-0.0108
0.41	-0.1581	-0.0092	-0.0093	-0.0095	-0.0097
0.42	-0.1402	-0.0081	-0.0083	-0.0084	-0.0086
0.43	-0.1224	-0.0071	-0.0072	-0.0074	-0.0075
0.44	-0.1047	-0.0061	-0.0062	-0.0063	-0.0064
0.45	-0.0871	-0.0051	-0.0051	-0.0052	-0.0054
0.46	-0.0696	-0.0040	-0.0041	-0.0042	-0.0043
0.47	-0.0522	-0.0030	-0.0031	-0.0031	-0.0032
0.48	-0.0347	-0.0020	-0.0021	-0.0021	-0.0021
0.49	-0.0174	-0.0010	-0.0010	-0.0010	-0.0011
0.50	±0.0000	±0.0000	±0.0000	±0.0000	±0.0000
0.51	$+0.0174$	$+0.0010$	$+0.0010$	$+0.0010$	$+0.0011$
0.52	$+0.0347$	$+0.0020$	$+0.0021$	$+0.0021$	$+0.0021$

For values beyond $\alpha = 0.50$ the table progresses inversely as above but with sign $+$. Example: $\alpha = 0.53$, $(1 - \alpha = 0.47)$, read row for $\alpha = 0.47$, i.e., log $\dfrac{\alpha}{1-\alpha} = +0.0522$, etc. If $\alpha = 0.80$, $(1 - \alpha = 0.20)$, read row for $\alpha = 0.20$, i.e., log $\dfrac{\alpha}{1-\alpha} = +0.6021$, etc.

TABLE G
DISSOCIATION EXPONENTS OF ACIDS

Important: *Values are to be regarded as approximate. It is impracticable to state conditions in every case. Note distinction between pK and pK'.*

ACID	pK'	AUTHOR-ITY	ACID	pK'	AUTHOR-ITY
Acetic..................pK	4.73*	(4)	Malonic....................	2.80	(1)
Alloxan.....................	6.6	(3)	Malonic 2d................	5.68	(1)
Arsenic.....................	2.3	(3)	Mucic.....................	3.2	(6)
Arsenic 2d..................	4.4	(3)	Nitrous....................	3.4	(3) 18°
Arsenic 3d..................	9.2	(3)	Oxalic.....................	1.42	(1)
Arsenious..................	9.2	(3)	Oxalic 2d..................	4.39	(6)
Azelaic.....................	4.6	(1)	Phenol.....................	10.0	(3)
Azelaic 2d.................	5.6	(6) 18°	Phosphoric...........pK₁	2.11*	(10)
Barbituric.................	4.0	(3)	Phosphoric...........pK₂	7.16*	(9)
Benzoic....................	4.2	(3)	Phosphoric...........pK₃	12.66*	(10)
Boric......................	9.2	(3)	o-phthalic.................	2.92	(1)
Butyric....................	4.8	(3)	o-phthalic 2d..............	5.41	(1)
Carbonic..............pK₁	6.33*	(5)	m-phthalic.................	3.54	(1)
Carbonic..............pK₂	10.22*	(5)	m-phthalic 2d.............	4.62	(1)
Citric.....................	3.08	(8)	Pimelic....................	2.92	(1)
Citric 2d..................	4.39	(8)	Pimelic 2d................	5.41	(1)
Citric 3d..................	5.49	(8)	Propionic..................	4.8	(3)
Formic....................	3.7	(3)	Pyrotartaric...............	4.1	(6)
Fumaric...................	3.03	(1)	Pyrotartaric 2d...........	5.63	(2)
Fumaric 2d................	4.49	(1)	Salicylic...................	3.0	(3)
Glucose...................	12.3	(3)	Sebacic....................	4.62	(1)
Glutaric...................	4.32	(1)	Sebacic 2d................	5.60	(1)
Glutaric 2d................	5.54	(1)	Succinic...................	4.18	(1)
Hippuric...................	3.7	(3)	Succinic 2d...............	5.57	(1)
Hydrocyanic...............	9.1	(3)	Sulfanilic..................	3.2	(3)
Hydrogen sulphide.........	7.2	(3) 18°	Sulfurous..................	1.8	(3)
Hydrogen sulphide 2d......	14.7	(7) 0°	Sulfurous 2d..............	5.3	(3)
Itaconic...................	3.8	(6)	Mono brom succinic.......	2.56	(1)
Itaconic 2d................	5.7	(6)	Mono brom succinic 2d....	4.41	(1)
Lactic.....................	3.85	(6)	d-Tartaric.................	3.0	(6)
Maleic.....................	1.93	(1)	d-Tartaric 2d..............	4.39	(2)
Maleic 2d..................	6.58	(1)	Thiodiglycollic............	3.31	(6)
1-malic....................	3.48	(6)	Thiodiglycollic 2d.........	4.46	(2)
1-malic 2d.................	5.11	(2)	Uric......................	5.8	(6) 18°

* pK value.

Authorities

(1) Chandler (1908) 25°.
(2) Larsson (1922) 18°.
(3) Landolt-Börnstein (1923) 25°.
(4) Cohn, Heyroth and Menkin (1928) see page 509.
(5) Hastings and Sendroy (1925). $pK_1' = 6.33 - 0.5 \sqrt{\mu}$ at 38°. $pK_2' = 10.22 - 1.1 \sqrt{\mu}$ at 38°.
(6) Scudder (1914) 25°.
(7) Jellinek and Czerwinski (1922).
(8) Hastings and Van Slyke (1922).
(9) Cohn (1927). $pK_2' = 7.16 - \dfrac{1.5 \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}} + K_S\mu$ (see page 506).
(10) Sendroy and Hastings (1927). $pK_1' = 2.11 - 0.5 \sqrt{\mu}$ at 18°. $pK_2' = 12.66 - 2.25 \sqrt{\mu}$ at 38°.

TABLE H

Dissociation Constants and Association Exponents of Bases

$$\frac{[B^+]\,[OH^-]}{[BOH]} = K_b \qquad \frac{[B]\,[H^+]}{[\overset{+}{BH}]} = K_{ab} \qquad pK_{ab} = \log\frac{1}{K_{ab}}$$

Assumptions:

$$pK_{ab} = K_w - pK_b$$

Values of K_w taken from table 6, page 45
Values of K_b taken from Kolthoff and Furman (1926)

BASE	K_b TEMPERATURE °C.	pK_{ab}
Ammonia....................	1.75×10^{-5} $18°$	9.37
Aniline.......................	4.6×10^{-10} $25°$	4.56
Ethylamine...................	5.6×10^{-4} $25°$	10.64
Diethylamine.................	1.26×10^{-3} $25°$	11.00
Triethylamine.................	6.4×10^{-4} $25°$	10.70
Methylamine..................	5.0×10^{-4} $25°$	10.59
Dimethylamine...............	7.4×10^{-4} $25°$	10.76
Trimethylamine...............	7.4×10^{-5} $25°$	9.76
Pyridine.....................	2.3×10^{-9} $25°$	5.26
Urea.........................	about $(1.5 \times 10^{-14}$?$)$	(0.1)

TABLE I

DISSOCIATION EXPONENTS AND ASSOCIATION EXPONENTS OF AMINO ACIDS AT 25°

(After Bjerrum (1923))

$$pK = \log \frac{1}{K} \qquad\qquad pK_w = 13.90$$

$$k_a = \frac{[NH_2RCOO^-][H^+]}{[NH_2RCOOH]} \qquad K_A = \frac{[NH_3^+RCOO^-][H^+]}{[NH_3^+RCOOH]}$$

$$k_b = \frac{[NH_3^+RCOOH][OH^-]}{[NH_2RCOOH]} \qquad K_B = \frac{[NH_3^+RCOO^-][O\overline{H}]}{[NH_2RCOO^-]}$$

			pk_a	$pK_w - pK_b$	pK_A	$pK_w - pK_B$
Aliphatic:						
Glycine			9.75	2.33	2.33	9.75
Methyl glycine			9.89	2.15	2.15	9.89
Dimethyl glycine			9.85	1.93	1.93	9.85
Betaine			$ca14$	1.34	1.34	$ca14$
Alanine			9.72	2.61	2.61	9.72
Leucine			9.75	2.26	2.26	9.75
Phenylalanin			8.60	2.01	2.01	8.60
Tyrosine			8.40	2.51	2.51	8.40
Glycyl glycine			7.74	3.20	3.20	7.74
Alanyl glycine			7.74	3.20	3.20	7.74
Leucyl glycine			7.82	3.38	3.38	7.82
Taurine			8.8	$ca0$	$ca0$	8.8
Asparagine			8.87	2.08	2.08	8.87
Lysine	First step		12	<6.94	1.94	12
	Second step		—	1.94	—	6.94
Arginine	First step		>13.96	6.9	2.24	$ca14$
	Second step		—	2.24	—	7.0
Histidine	First step		8.66	5.66	1.60	8.66
	Second step		—	1.60	—	5.66
Aspartic acid	First step		3.82	1.98	1.98	12.1
	Second step		12.1	—	3.82	—
Aromatic:						
o-amino benzoic			4.98	2.04	2.04	4.98
m-amino benzoic			4.92	3.27	3.27	4.92
p-amino benzoic			4.80	1.98	1.98	4.80
o-benzbetaine			>14	1.98	1.98	-0.1
m-benzbetaine			>14	1.35	1.35	-0.1
p-benzbetaine			$ca14$	3.43	3.43	$ca-0.1$
o-amino benzene sulfonic acid			2.48	—	—	2.48
m-amino benzene sulfonic acid			3.73	—	—	3.73
p-amino benzene sulfonic acid			3.24	—	—	3.24

TABLE J

ALKALOIDS—HALF TRANSFORMATION POINTS AT 15°C. AS DETERMINED
ROUGHLY BY KOLTHOFF (1925)

$$pK = 14.2 - \log \frac{1}{K_b}$$

ALKALOID	pK'	ALKALOID	pK$_2'$	pK$_1'$
Aconitine.............	8.32	Brucine..............	8.16	2.50
Atropine.............	9.85	Cinchonine.........	8.35	4.28
Cocaine..............	8.61	Emetine............	8.43	7.56
Codeine..............	8.15	Nicotine............	8.04	3.24
Coniine..............	11.10	Novocaine..........	9.05	2.47
Morphine.............	8.07	Quinine.............	8.23	4.50
Thebaine.............	8.15	Strychnine..........	8.20	2.50

TABLE K

RELATION OF PERCENTAGE REDUCTION TO POTENTIAL AT CONSTANT pH

DETERMINED BY $E_h = E'_o - 0.03006 \log \dfrac{[Sr]}{[So]}$ AT 30°C.

(Values rounded to nearest millivolt)

REDUCTION	$-0.03006 \log \dfrac{[Sr]}{[So]}$	REDUCTION	$-0.03006 \log \dfrac{[Sr]}{[So]}$
per cent	*volts*	*per cent*	*volts*
1	+0.060	55	−0.003
2	0.051	60	0.005
5	0.038	65	0.008
10	0.029	70	0.011
15	0.023	75	0.014
20	0.018	80	0.018
25	0.014	85	0.023
30	0.011	90	0.029
35	0.008	95	0.038
40	0.005	98	0.051
45	+0.003	99	−0.060
50	±0.000		

TABLE L
E_o' Values for Several Oxidation-Reduction Indicators, 30°C.
(Values rounded to nearest millivolt)

pH	INDIGO DISULPHONATE	INDIGO TRISULPHONATE	INDIGO TETRASULPHONATE	METHYLENE BLUE	TOLUYLENE BLUE	1-NAPHTHOL-2-SULPHONATE INDO, 3' 5' DICHLORO-PHENOL	1-NAPHTHOL-2-SULPHONATE INDOPHENOL	2, 6-DICHLOROPHENOL INDO O-CRESOL	2, 6-DICHLOROPHENOL INDO-PHENOL	BINDSCHEDLER'S GREEN	O-CHLOROPHENOL INDO-PHENOL	M-BROMOPHENOL INDO-PHENOL
5.0	−0.010	0.032	0.065	0.101	0.221	0.262		0.335	0.366	0.335		
5.2	0.022	0.020	0.053	0.088	0.208	0.249		0.322	0.352	0.320		
5.4	0.034	+0.008	0.041	0.077	0.196	0.236	*	0.307	0.339	0.307	*	*
5.6	0.045	−0.004	0.029	0.066	0.184	0.223		0.292	0.325	0.293		
5.8	0.057	0.016	0.017	0.056	0.173	0.210		0.277	0.310	0.281		
6.0	0.069	0.028	+0.006	0.047	0.162	0.196	0.183	0.261	0.295	0.270	0.301	
6.2	0.081	0.039	−0.006	0.039	0.151	0.181	0.171	0.245	0.279	0.259	0.288	
6.4	0.092	0.051	0.017	0.031	0.141	0.166	0.159	0.228	0.263	0.249	0.275	*
6.6	0.104	0.061	0.027	0.024	0.132	0.150	0.147	0.212	0.247	0.240	0.262	
6.8	0.114	0.072	0.037	0.017	0.123	0.134	0.135	0.196	0.232	0.232	0.248	
7.0	0.125	0.081	0.046	0.011	0.115	0.119	0.123	0.181	0.217	0.224	0.233	0.248
7.2	0.134	0.091	0.055	+0.004	0.108	0.103	0.111	0.166	0.203	0.217	0.218	0.235
7.4	0.143	0.099	0.062	−0.002	0.101	0.088	0.099	0.152	0.189	0.210	0.203	0.221
7.6	0.152	0.107	0.070	0.008	0.094	0.073	0.087	0.138	0.175	0.204	0.187	0.208
7.8	0.160	0.114	0.077	0.014	0.088	0.060	0.074	0.125	0.162	0.197	0.170	0.193
8.0	0.167	0.121	0.083	0.020	0.082	0.046	0.062	0.112	0.150		0.155	0.178
8.2	0.174	0.127	0.090	0.026	0.075	0.034	0.049	0.099	0.137		0.139	0.163
8.4	0.180	0.134	0.096	0.032	0.069	0.021	0.026	0.087	0.125		0.124	0.148
8.6	0.187	0.140	0.102	0.038	0.063	+0.010	0.023	0.075	0.113	†	0.109	0.133
8.8	0.193	0.146	0.108	0.044	0.057	−0.002	+0.010	0.063	0.101		0.095	0.117
9.0	−0.199	−0.152	−0.114	−0.050	0.051	−0.012	−0.003	0.051	0.089		0.082	0.103

* Unstable in this region of pH.

† Decomposes in this region of pH.

TABLE M

SYMBOLS AND CONVENIENT FORMULAS

For notation see definitions in text as a notation is introduced

(A)   Read: The activity of A.

[A]   Read: The concentration of A in moles per liter, unless otherwise specified.

$\cong$ Read: Is approximately or essentially equal to.

$=$ Read: Is equal to.

$\equiv$ Read: Is identical with.

$>$ Read: Is greater than.

$<$ Read: Is less than.

$\int$ Symbol of integration.

Σ Read: The sum of all terms following.

Δ Read: The increment of.

$||$ Read: Liquid junction potential is here considered to be eliminated or otherwise allowed for.

$|$ Read: There is a potential difference here.

$\}$ Read: There is a junction potential here and the junction is a flowing junction.

ln Read: Logarithm to the base e.

log Read: Logarithm to the base 10.

$log \; x = 0.43429 \; ln \; x$

$ln \; x = 2.3026 \; log \; x$

d Read: The infinitesimal increment of or differential of.

$$\frac{d(a^v)}{d \; x} = a^v \; ln \; a \; \frac{d \; v}{d \; x} \; .$$

$pH \equiv log \dfrac{1}{[H^+]}$ (formally).   For the experimental meaning see Chapter XXIII.

$pK \equiv log \dfrac{1}{K}$ (formally).   For experimental meaning compare with pH.

See also subject index.

TABLE N

DEFINITIONS (OF LESS COMMON TERMS) WHICH ARE USED AND NOT INCLUDED IN THE TEXT

Definitions are the most accursed of all things on the face of the earth.—R. HUNTER.

I. C. T. refers to *International Critical Tables*.

Dimensions are enclosed in [ ].

Ampere.—Unit of electric current. Abs. ampere = 0.1 cgs. unit. Int. ampere is that unvarying electric current which, when passed through a solution of silver nitrate in water, in accordance with certain specifications, deposits silver at the rate of 0.00111800 gram per second. *I. C. T.*

Ångstrom unit.—($\mathring{A}$). [l]. 10^{-10} meters. International Ångstrom defined as such a length that wave-length of red cadmium line in air at 15°C., A_n, is exactly 6438.4696 Int. $\mathring{A}$; it = 10^{-10} m within experimental error. *I. C. T.*

Anion.—An ion with net excess negative charge causing it to travel toward the anode (+) in electrolysis.

Anode.—See *electrode*.

Atmosphere.—[force area^{-1}], [m/lt^2]. 1. Normal atmosphere (A_n) defined as pressure exerted by vertical column of liquid 76 cm. long, density 13.5951 grams per cm.^{3}, acceleration of gravity being 980.665 cm. sec.$^{-2}$. 2. Atmosphere at 45° (A_{45}) differs from A_n only in use of acceleration of gravity at sea level and lat. 45° instead of 980.655 cm. sec.$^{-2}$. 3. British atmosphere is based on 30 inches instead of 76 cm. *I. C. T.*

Avogadro's number.—(N_o), [m^{-1}]. Number of molecules in a mole. *I. C. T.*

Calorie.—[Heat], [ml^2/t^2]. 1. Heat per unit of mass, per °C. of rise, required to produce small rise in temperature of water under pressure A_n; varies with temperature, which must be stated. If unit of mass is gram, it is called small calorie, gram calorie, or calorie; symbol is cal. If unit of mass is kilogram, it is called large calorie, kilogram calorie, or Calorie; symbol, Cal. (2) Mean calorie = 1/100 of heat required to raise unit mass of water from 0° to 100°C., pressure A_n. *I. C. T.*

Cation.—An ion with net excess positive charge causing it to travel toward the cathode (−) in electrolysis.

Cathode.—See *electrode*.

Colligative properties.—"The properties of solutions are determined, not by the relative weights of the substances present, but rather by the relative number of molecules of the constituents present in the solution. Such properties of solutions have been designated by Ostwald as colligative properties." Frazer, p. 235, Taylor's Treatise.

Conductance.—Reciprocal of resistance. *I. C. T.*

Conductivity, Electrical.—Reciprocal of electrical resistivity (q.v.). 1. (κ) Volume conductivity = reciprocal of volume resistivity; specific conductance. 2. Mass conductivity = κ/d; d = density. 3. Equivalent conductivity (Λ) is κ/c; c = equivalents of solute per unit volume of solution. 4. Molecular conductivity (μ) is κ/m; m = moles of solute per unit volume of solution. *I. C. T.*

Coulomb.—The quantity of electricity transferred in one second by a current of one ampere. *I. C. T.*

Dielectric constant.—(ϵ) (or D) [t^2/μl^2], [ϵ]. The force (f) of repulsion between two point charges (e, e') of electricity at a distance (r) apart in a uniform medium of great extent is $f = ee'/\epsilon r^2$; ϵ depends upon the nature of the medium, and is called its dielectric constant. *I. C. T.*

Dichromatism.—From $\delta\iota$-(two) and $\chi\rho\hat{\omega}\mu\alpha$ (color).

Dyne.—[ml/t²].   The cgs. unit of force.   The force which, when acting continuously upon a mass of one gram and not opposed by another, will impart to the mass a uniform acceleration of one cm. per sec.².   *I. C. T.*

Electromotive force.—(E), (E. M. F.).   See Potential.

Electron.—Negative electrons are very small negatively charged particles observed under many, very diverse conditions.   All appear to be alike in every way, including amount of charge carried.   They appear to be one of the basic elements of which atoms are made.   *I. C. T.*

Applied by G. J. Stoney (1891) to the electric charge associated with each "bond" in one chemical atom.

Electrolytes.—"Many bodies are decomposed directly by the electric current, their elements being set free; these I propose to call electrolytes."   Faraday in 1834.

Electrode.—"In place of the term pole, I propose using that of *electrode*, and I mean thereby that substance, or rather surface, whether of air, water, metal or any other body, which bounds the extent of the decomposing matter in the direction of the electric current.   If a system is so oriented with respect to the points of the compass that what is called the positive current enters at the east and departs at the west (the direction of the sun's apparent motion) the **anode** (up way) is that surface at which the electric current according to our present expression enters.   The **cathode** (down way) is that surface at which the current leaves the decomposing body."   Faraday in 1834.

Equivalent.—(equiv.).   Electrochemical equivalent (briefly equivalent) of an ion—actual or potential—is its formula weight divided by its valence.   *I. C. T.*

Erg.—[force . distance], [ml²/t²].   Work done by a force of one dyne while acting through a distance of one centimeter in its own direction.   *I. C. T.*

Faraday.—(F).   The electrical charge carried in electrolysis by one gram-equivalent.

Field.—The field of a physical quantity is the region of space within which phenomena characteristic of the quantity exist.   The strength, or intensity, of the field at any point is measured by the magnitude at that point of some chosen, characteristic phenomenon, and the complete designation of the field includes an indication of this phenomenon; *e.g.*, electrical field of force.   As force is the phenomenon most frequently chosen, and in other cases the context indicates what is intended, the explicit designation of the chosen phenomenon is quite frequently omitted.   *I. C. T.*

Force.—[ml/t²].   That which imparts acceleration to material bodies.   *I. C. T.*

Gas, Ideal.—One which strictly satisfies the equation ($pv = RTm$) and other relations deduced from the classical kinetic theory of gases on the assumption that the molecules are infinitely small and devoid of mutual attraction. *I. C. T.*

Gravity, Acceleration of.—(g), (g_s), [l/t^2]. Unless the contrary is indicated, this expression refers specifically to the earth, and denotes the resultant acceleration downward experienced by a freely falling body placed at the point considered. It includes centrifugal effects arising from the rotation of the earth, as well as the effects of gravitational attraction (*cf.* Gravity, standard). *I. C. T.*

Hydrion.—Proposed by Walker (1901) to replace the name "hydrogen ion," for H^+.

International electrical units.—A system of electrical and magnetic units based upon the ohm, the ampere, and secondarily upon the volt, all as realized by certain concrete standards which have been internationally agreed upon, and upon the cgs. units for such other quantities as may be involved. The concrete standards have been so chosen as to make the international system nearly identical with the practical system; as now defined, the outstanding discrepancy in no case exceeds 52 parts in 100,000. In distinguishing between the two systems, the units of the practical system are described as absolute, those of the other, as international. The introduction of the volt as a secondary unit defined by a concrete standard (Weston normal cell = 1.018300 Int. volts at 20°C.) introduces confusion when measurements of high precision are to be recorded. In these Tables, values based upon the Int. ohm and the Int. ampere (as defined by the silver voltameter) are denoted by (a). Those based on the Int. ohm and the Int. volt (as defined by the standard cell) are denoted by (v). *I. C. T.*

Ion.—From ἰών, "a traveller," is the general term for a substance which, by reason of a net excess positive or negative charge or charges, travels in an electric field.

Ionogen.—A term proposed by Alexander Smith (1901) for a material which is capable of forming ions.

Isobestic point.—A point of equal "quenching," or, as applied in spectrophotometry, of equal extinction.

Isohydric solutions.—Solutions of the same hydrion concentration, or activity (according to use).

Joule.—[ml^2/t^2]. 1. Absolute joule = 10^7 ergs. 2. International joule = work expended per second by an Int. ampere in an Int. ohm. *I. C. T.*

Kilo-.—Prefix denoting 1,000. *I. C. T.*

Mega-.—Prefix = 1,000,000. *I. C. T.*

Micro-.—Prefix denoting $1/10^6$. *I. C. T.*

Micron.—(μ). Unit of length = 1/10. m^6 = 0.001 mm. *I. C. T.*

Milli-.—Prefix = 0.001. *I. C. T.*

Mobility (of ions in solution).—At infinite dilution the equivalent conductance, Λ_∞, was stated by Kohlrausch to be the sum of two effects, one due to the anions, the other to the cations. Kohlrausch called these the mobilities and defined the mobilities of the anions and cations, V and U, respectively, by the relation $\Lambda_\infty = V + U$.

Molality.—The number of moles of a solute in 1000 grams of solvent.

Molarity.—The number of moles of a solute in 1 liter of solution.

Mole.—A variable, derived unit of mass: its mass is numerically equal to the molecular weight of the substance measured. The expressions gram-mole, kilogram-mole, etc. are used to designate the basic unit of mass employed. Similarly derived units based upon the atomic weight, the formula weight, or the equivalent are called the gram-atom, gram-formula weight or gram-equivalent when the gram is the basic unit, and correspondingly in other cases. *I. C. T.*

Molecular weight.—(M). The sum of atomic weights of all the atoms contained in a molecule. *I. C. T.*

Normal.—A concentration of one gram-equivalent per liter. *I. C. T.*

Ohm.—(Ω). A unit of electrical resistance. 1. Absolute ohm $= 10^9$ cgsm. units. 2. International ohm is the resistance, at the temperature of melting ice, offered to an unvarying electric current by a column of mercury, of constant sectional area, having a mass of 14.4521 grams and a length, at the temperature mentioned, of 106.300 cm. *I. C. T.*

Percent.—(%). The number of units of the constituent in 100 units of the mixture containing it. If units of volume are used, the ratio is called volume per cent; if units of mass, it is called mass per cent, weight per cent, or simply per cent. (% must be distinguished from ‰ which is frequently used to denote per thousand.)—*I. C. T.*

Phase.—"A phase is any part of a system, which is homogeneous throughout; it is bounded by a surface and is mechanically separable from the other parts of the system." Hill in Taylor's Treatise, p. 370.

Potential.—The excess of the potential at the point A over that at B, with reference to any quantity m, is the mechanical work per unit of m which must be done in carrying a very small positive amount of m from B to A. The difference in electrical potential is called **electromotive force, emf,** E. M. F., **potential difference**; in magnetic potential, is called magnetomotive force, mmf. *I. C. T.*

Potential gradient.—The space rate of increase in the potential. If the direction in which the rate to be measured is not stated, that corresponding to the maximum gradient is to be understood. *I. C. T.*

Power.—The time rate of doing work.

Pressure.—(p), (P). [m/lt²]. Normal force per unit of area. A hydrostatic pressure is a pressure which is the same in all directions. *I. C. T.*

Quadrant.—1. Unit of angle $= 90°$. *I. C. T.*

Resistance.—1. The electrical resistance of a body between two specified equipotential surfaces is E/I, where E is the unchanging difference in the potentials of the surfaces and I is the resulting current across any transverse section between them. 2. Specific resistance. *I. C. T.*

Solute.—A component of a solution present in amount smaller than that of the solvent.

Solvent.—The component of a solution present in the largest amount.

Spectrum.—"The spectrum is a graphic arrangement or setting in order of radiant energy with respect to wave-length or frequency." Rept. Optical Soc.

Stoichiometric.—Pertaining to the ratio of the masses of the several elements contained in a pure chemical compound. *I. C. T.*

A term introduced by Richter to denote the determination of the relative amounts in which acids and bases neutralize one another.

Transport number (of ions in solution).—"If in electrolysis one equivalent of kation is deposited, a fraction n is taken from the immediate vicinity of the electrode, and the fraction $(1 - n)$ migrates into the kathode space from the bulk of the solution. Thus n equivalents of anion must migrate out of the kathode space to make up the total charge F crossing any section of the electrolyte. The current is carried by anions and kations in the ratio $\dfrac{n}{1 - n}$. The fraction n was called by Hittorf the *transport number* of the anion. The transport number of the kation is $1 - n$." See Partington in Taylor's Treatise, p. 543.

Volt.—The electrical potential difference which, when steadily applied to a conductor having a resistance of one ohm, will produce in it a current of one ampere (*cf.* absolute and international units). The Int. Committee authorized by the London Conference, 1908, agreed to regard the emf of the Weston normal cell at 20°C. as exactly 1.0183 Int. volts. This furnishes a subsidiary definition which is slightly discordant with the primary one. These tables distinguish between the two, and between units derived from them, by using (a) to denote those based on ampere and ohm, and (v) to denote those based on volt as defined by the Weston cell. *I. C. T.*

Wave-length.—(λ). Distance between consecutive corresponding points in a monofrequent wave train. Occasionally applied to complex waves. *I. C. T.*

Weight.—The force with which a body, left to itself, is urged towards the earth. In the absolute systems of units it is numerically equal to the mass of the body multiplied by the acceleration of gravity (g) at the position considered; hence varied with position. Such expressions as gram weight [pound weight] are to be interpreted as meaning the weight of a gram [a pound] at a place where g has the standard value, 980.665 cm./sec.[2] *I. C. T.*

NATURAL NUMBERS	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	49C0	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5052	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

NATURAL NUMBERS	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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INDEX OF SUBJECTS

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Sans Tache

Sans Tache

IN THE "elder days of art" each artist or craftsman enjoyed the privilege of independent creation. He carried through a process of manufacture from beginning to end. The scribe of the days before the printing press was such a craftsman. So was the printer in the days before the machine process. He stood or fell, as a craftsman, by the merit or demerit of his finished product.

Modern machine production has added much to the worker's productivity and to his material welfare; but it has deprived him of the old creative distinctiveness. His work is merged in the work of the team, and lost sight of as something representing him and his personality.

Many hands and minds contribute to the manufacture of a book, in this day of specialization. There are seven distinct major processes in the making of a book: The type must first be set; by the monotype method, there are two processes, the "keyboarding" of the MS and the casting of the type from the perforated paper rolls thus produced. Formulas and other intricate work must be hand-set; then the whole brought together ("composed") in its true order, made into pages and forms. The results must be checked by proof reading at each stage. Then comes the "make-ready" and press-run and finally the binding into volumes.

All of these processes, except that of binding into cloth or leather covers, are carried on under our roof.

The motto of the Waverly Press is *Sans Tache*. Our ideal is to manufacture books *"without blemish"*—worthy books, worthily printed, with worthy typography—books to which we shall be proud to attach our imprint, made by craftsmen who are willing to accept open responsibility for their work, and who are entitled to credit for creditable performance.

The printing craftsman of today is quite as much a craftsman as his predecessor. There is quite as much discrimination between poor work and good. We are of the opinion that the individuality of the worker should not be wholly lost. The members of our staff who have contributed their skill of hand and brain to this volume are:

Keyboard: Katharine Kocent, Mildred Lambert, Louise Hilpert, Helen Twardowicz, Anna Rustic, Hannah Scott, Laurel Tourtellotte.

Casters: Kenneth Brown, Ernest Wann, Charles Aher, Mahlon Robinson, George Smith, Martin Griffen, Henry Lee, Charles Fick, George Bullinger, Norwood Eaton.

Composing Room: John Crabill, James Jackson, Anthony Wagner, Herbert Leitch, William Sanders, Henry Johansen, Harry Harmeyer, George Moss, Austin Uhland, Ray Kauffman, Andrew Rassa, James Armiger, Ernest Salgado, Charles Wyatt, Arthur Baker, Edward Rice, Richard King, Henry Shea, Theodore Nilson.

Proof Room: Sarah Katzin, Mary Reed, Alice Reuter, Ruth Jones, Lucile Bull, Audrey Tanner, Ethel Strasinger, Dorothy Strasinger, Angeline Eifert, Ida Zimmerman, Shirley Seidel, Lillian Gilland.

Press: Andrew Becker, Fred Lucker, August Hildebrand, Leo Ledlich, William Harrison, Jr., Thomas Shreck, Robert Gallagher, Raymond Gallagher.

Cutter: William Armiger.

Folders: Laurence Krug, Shipley Dellinger.